

Application No.: 10/583,220
Appeal Brief Dated: February 6, 2012
Reply to Office Action of: May 5, 2011

JFE-117US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appln. No: 10/583,220
Applicant: Atsushi Miyazaki et al.
Filed: June 16, 2006
Title: FERRITIC Cr-CONTAINED STEEL
T.C./A.U.: 1733
Examiner: Caitlin Anne Kiechle
Confirmation No.: 7655
Docket No.: JFE-117US

APPEAL BRIEF UNDER 37 C.F.R. § 41.37

MAIL STOP APPEAL BRIEF - PATENTS

Commissioner for Patents
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S I R :

Appellants hereby request consideration and reversal of the Final Rejection dated **May 5, 2011**, of claims 13-17, 20, and 21.

This Brief is presented in the format required by 37 C.F.R. § 41.37, in order to facilitate review by the Board. In compliance with 37 C.F.R. § 41.37(a)(1), this Brief is being filed within the time allowed for response to the action from which the Appeal was taken or within two months from the date of the Notice of Appeal, whichever is later, and with any necessary extensions of time.

The fees for filing a Brief in support of an Appeal under 37 C.F.R. § 41.20(b)(2), together with any extension fee required in connection with the filing of this Brief, are provided herewith.

I. REAL PARTY IN INTEREST

The real party in interest is JFE Steel Corporation.

II. RELATED APPEALS AND INTERFERENCES

There are no appeals or interferences related to the subject matter of this Appeal.

III. STATUS OF CLAIMS

Claims 13-33 are pending in the above-referenced application, with claims 18, 19, and 22-33 withdrawn from consideration. Claims 1-12 were previously cancelled. Claims 13-17, 20, and 21 stand rejected, and are being appealed.

IV. STATUS OF AMENDMENTS

The present application is under Final Rejection. All previous Amendments have been entered.

V. SUMMARY OF CLAIMED SUBJECT MATTER

The present invention relates to a ferritic Cr-contained steel. With respect to Appellants' claim 13, a ferritic Cr-contained steel is claimed. (See, e.g., Specification at ¶ 5, page 3, line 21.) A cold rolled annealed sheet is annealed, after cold rolling, at a final annealing temperature at 1050 to 1200°C. (See, e.g., Specification at ¶ 34, page 11, lines 23-25.) The steel comprises C of about 0.03% or less, Mn of about 5.0% or less, Cr of about 6 to about 40%, N of about 0.03% or less, and Si of about 5% or less in percent by mass. (See, e.g., Specification at ¶ 5, no. 1, page 3, lines 21-23.) The steel also comprises W of about 2.05 to about 6.0% in percent by mass. (See, e.g., Specification at ¶ 5, no. 1, page 3, line 22, and Table 1.) The remainder of the steel comprises Fe and inevitable impurities. (See, e.g., Specification at ¶ 5, no. 1, page 3, lines 22-23.) Precipitated W is 0.005% to 0.1% in percent by mass. (See, e.g., Specification at ¶ 5, no. 1, page 3, lines 23-24, and ¶ 23, page 8, lines 24-26.) An average thermal expansion coefficient between 20°C and 800°C is less than about $12.6 \times 10^{-6}/^{\circ}\text{C}$. (See, e.g., Specification at ¶ 5, no. 1, page 3, lines 24-25.)

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VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

Whether claims 13-17, 20, and 21 are properly rejected under 35 U.S.C. § 103(a) as unpatentable over Kawabata et al. (US 5,626,694). Whether claims 13-17, 20, and 21 are properly rejected on the ground of non-statutory double patenting as unpatentable over claims 1-8, 10-14, and 16 of U.S. Patent No. 7,806,993 in view of Kawabata et al.

VII. ARGUMENT

A. OVERVIEW OF ARGUMENTS

This Appeal focuses on the Office's reliance on alleged inherent disclosures of two claim limitations by the prior art as a basis for its rejections. Appellants seek reversal of the rejections based on evidence showing (1) that the Office has not established *prima facie* obviousness and (2) that a *prima facie* case of obviousness (even if made) has been rebutted.

The rejections allege that one of skill would expect the steel of Kawabata et al. to inherently have two features—Appellants' claimed precipitated W % and Appellants' claimed average thermal expansion coefficient. The rejections are made under the standard of MPEP 2112, which requires that the claimed and prior art products are identical or substantially identical in terms of composition or process. Evidence of record clearly shows, however, that the steel products of Appellants and Kawabata et al. differ substantially in their respective compositions and their respective manufacturing processes. Thus, the standard for establishing inherency has not been met, *prima facie* obviousness has not been established, and a burden to establish non-obviousness has not shifted to Appellants.

Assuming *arguendo* that the Office has established *prima facie* obviousness though it has not, evidence of record clearly rebuts alleged obviousness based on inherency under the standard of MPEP 2112. Specifically, evidence of record establishes that the steel of Kawabata et al. does not necessarily possess Appellants' claimed precipitated W % or Appellants' claimed average thermal expansion coefficient. Thus, Kawabata et al. does not inherently disclose Appellants' claimed precipitated W % or Appellants' claimed average thermal expansion coefficient, and *prima facie* obviousness (even if established) has been successfully rebutted by Appellants.

The Office has not yet addressed the evidence cited by Appellants in connection with alleged inherency under MPEP 2112. Despite the cited evidence, the Office has maintained its rejection and alleges that one of skill would have "expected" the steel of Kawabata et al. to have "a similar amount of precipitated W" and "a similar average thermal expansion coefficient." See Advisory Action dated September 21, 2011. Appellants request reversal of the rejection for the reasons set forth in the following sections of this Brief.

**B. REJECTION OF CLAIMS 13-17, 20, AND 21
AS UNPATENTABLE OVER KAWABATA ET AL.**

Claims 13-17, 20, and 21 stand rejected as unpatentable over Kawabata et al. Appellants submit that this rejection should be reversed for the reasons set forth in the following sections of this Brief: Section I addresses the appropriate standards required for establishing and rebutting *prima facie* obviousness under MPEP 2112; Section II addresses the Office's failure to establish *prima facie* obviousness; and Section III addresses evidence rebutting alleged *prima facie* obviousness.

I. THE REJECTION ALLEGES THAT APPELLANTS' CLAIMED PRECIPITATED W AND AVERAGE THERMAL EXPANSION COEFFICIENT LIMITATIONS WOULD BE EXPECTED IN THE STEEL OF THE KAWABATA ET AL. REFERENCE UNDER THE STANDARD OF MPEP 2112

This Section I addresses the rationale of the current rejection and the standards required for establishing and rebutting *prima facie* obviousness under MPEP 2112.

Claim 13 recites (among others) the following limitations:

- 1) precipitated W is 0.005% to 0.1 % in percent by mass; and
- 2) average thermal expansion coefficient between 20°C and 800°C is less than about $12.6 \times 10^{-6}/^{\circ}\text{C}$.

The inventors discovered that the addition of W to the Fe--Cr ferritic alloys and a decrease in the amount of precipitated W remarkably contributed to a decrease in thermal expansion coefficient of the alloys. While the reason for this is not clear, Appellants believe it is because of several points. The first point is that, while grain boundaries essentially act as a cushion for thermal expansion, since the Laves phase is precipitated therein, the cushion effect is reduced, and consequently the thermal expansion coefficient is increased. The second point is that, when the amount of the precipitated W is increased in the alloy, the amount of solid soluted W is decreased, and consequently a decrease in the thermal expansion coefficient of the alloy is inhibited. However, even if the amount of precipitated W is slight, for example, only more than 0.1%, the decrease in thermal expansion coefficient of the alloy is

inhibited, therefore the reason cannot be explained only from the increase in the amount of dissolved W in the alloy. Thus, the first point, a decrease in effect as a cushion of the grain boundaries, is considered to be major. See Appellants' substitute specification at paragraphs 0003 and 0004 (in Evidence Appendix).

As discussed in the following sections, the Office's rejection alleges that Appellants' claimed precipitated W % and average thermal expansion coefficient would be expected in the steel of the Kawabata et al. reference under the standard of MPEP 2112. To be proper, such a rejection requires a showing that the claimed and prior art products are identical or substantially identical in structure or composition or are produced by identical or substantially identical processes. Also, such a rejection (even if proper) can be rebutted by evidence showing that the prior art products do not necessarily possess the characteristics of the claimed product.¹

- a) THE OFFICE'S REJECTION ALLEGES THAT APPELLANTS' CLAIMED PRECIPITATED W % AND APPELLANTS' CLAIMED AVERAGE THERMAL EXPANSION COEFFICIENT WOULD BE EXPECTED BECAUSE THE COMPOSITION OF THE FERRITIC CR-CONTAINED STEEL OF KAWABATA ET AL. IS SAID TO OVERLAP WITH THE COMPOSITION OF THE STEEL OF THE INSTANT INVENTION AND BECAUSE THE STEEL OF KAWABATA ET AL. IS SAID TO BE MADE USING A METHOD SIMILAR TO THAT OF THE INSTANT INVENTION, CITING MPEP 2112

The sole rationale for the rejection of claims 13-17, 20, and 21, specifically with respect to Appellants' claimed precipitated W % and Appellants' claimed average thermal expansion coefficient, is set forth as follows:

¹ The rejection explicitly refers to inherency, which is consistent with the citation of MPEP § 2112 (titled Requirements of Rejection Based on Inherency; Burden of Proof). Whether or not the rejection refers to inherency, however, MPEP 2112 invokes principles of inherency. Accordingly, the associated legal standard, as stated in MPEP 2112(IV), requires that "the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art." (citing *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990)). Appellants note that the most recent statement of the Office's position (in the Advisory Action dated September 21, 2011) does not mention inherency and instead simply alleges that claimed limitations would have been "expected." Even if the rejection had not expressly referred to inherency and instead merely alleged that properties would be "expected," however, the question is still whether the allegedly inherent characteristic "necessarily flows from" the teachings of the applied prior art. In any event, the current rejection explicitly refers to inherency citing MPEP 2112.

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- Claims 13-17, 20, and 21 stand rejected as obvious based on Kawabata et al. (US 5,626,694) for the reasons set forth in the Office Action dated October 15, 2010.
- The Office acknowledged that Kawabata et al. does not expressly teach Appellants' claimed precipitated W and average thermal expansion coefficient limitations:

"Kawabata differs from instant claim 13 because it does not specifically teach that [1] the precipitated W is 0.005% to 0.1 mass% or that [2] average thermal expansion coefficient between 20°C and 800°C is less than about $12.6 \times 10^{-6}/^{\circ}\text{C}$." Office Action dated October 15, 2010, at page 3, last paragraph.

- Citing MPEP 2112, the Office Action concludes that "one of ordinary skill in the art would expect the steel of Kawabata to inherently have a similar amount of precipitated W and a similar average thermal expansion coefficient" because "the composition of the ferritic Cr-contained steel of Kawabata overlaps with the composition of the steel of the instant invention and since the steel of Kawabata is made using a method similar to the method of the instant invention." Office Action dated October 15, 2010, bridging pages 3 and 4.

Based on the record of this application and the foregoing excerpts of the Office Action, the current rejection of claims 13-17, 20, and 21 is based on the allegation that one would expect the steel of Kawabata to inherently have a similar amount of precipitated W and a similar average thermal expansion coefficient under the standard of MPEP 2112. No other rationale is provided in connection with these limitations.

b) MPEP 2112.01(I) REQUIRES A SHOWING THAT THE CLAIMED AND PRIOR ART PRODUCTS ARE IDENTICAL OR SUBSTANTIALLY IDENTICAL IN STRUCTURE OR COMPOSITION, OR ARE PRODUCED BY IDENTICAL OR SUBSTANTIALLY IDENTICAL PROCESSES

MPEP 2112 sets forth general standards required for establishing inherency of claimed subject matter that is not expressly disclosed in the prior art. Specifically:

- MPEP 2112(IV) requires that missing descriptive subject matter must necessarily be present in the thing described in the prior art reference:

"To establish inherency, the extrinsic evidence 'must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill"

- MPEP 2112(IV) also warns that inherency may not be established by mere possibilities:

"Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient." Citing *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999).

- MPEP 2112(IV) also requires that the Examiner must provide a basis in fact and/or technical reasoning in relying upon the theory of inherency:

"In relying upon the theory of inherency, the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art." Citing *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990) (emphasis in original).

- MPEP 2112.01(I) sets forth the following standard for establishing obviousness based on substantially identical compositions or processes:

"Where the claimed and prior art products are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a *prima facie* case of either anticipation or obviousness has been established. ... 'When the PTO shows a sound basis for believing that the products of the applicant and the prior art are the same, the applicant has the burden of showing that they are not.' ... Therefore, the *prima facie* case can be rebutted by evidence showing that the prior art products do not necessarily possess the characteristics of the

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claimed product." Citing *In re Best*, 562 F.2d at 1255, 195 USPQ at 433; *Titanium Metals Corp. v. Banner*, 778 F.2d 775, 227 USPQ 773 (Fed. Cir. 1985) (emphasis in original).

Accordingly, the issue is whether the Office has established *prima facie* obviousness under the standard of MPEP 2112 by showing a sound basis for believing that the claimed and prior art products are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes. In the terms of this application, the issue is whether the Office has shown a sound basis for believing that Appellants' claimed product and the product of Kawabata et al. are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes.

- c) UNDER MPEP 2112.01(I), A PRIMA FACIE CASE OF ANTICIPATION OR OBVIOUSNESS (IF MADE) CAN BE REBUTTED BY EVIDENCE SHOWING THAT THE PRIOR ART PRODUCTS DO NOT NECESSARILY POSSESS THE CHARACTERISTICS OF THE CLAIMED PRODUCT

MPEP 2112.01(I) sets forth the following standard for rebutting *prima facie* obviousness:

"[T]he *prima facie* case can be rebutted by evidence showing that the prior art products do not necessarily possess the characteristics of the claimed product." MPEP 2112.01(I) (citing *In re Best*, 562 F.2d at 1255, 195 USPQ at 433) (emphasis in original).

Accordingly, MPEP 2112.01(I) cites to *In re Best* for its specific standard for rebutting a case of *prima facie* obviousness that uses, as its rationale, similarities between prior art and claimed products and processes to account for a characteristic that is not expressly disclosed in the prior art (i.e., by showing that the prior art products do not necessarily possess the characteristics of the claimed product). In terms of this application, a *prima facie* case (if made) can be rebutted by evidence showing that the steel product of Kawabata et al. does not necessarily possess at least one of Appellants' claimed precipitated W limitation or Appellants' claimed average thermal expansion coefficient limitation.

II. THE OFFICE HAS NOT ESTABLISHED *PRIMA FACIE* OBVIOUSNESS AND THE BURDEN HAS NOT SHIFTED TO APPELLANTS TO ESTABLISH NON-OBVIOUSNESS

As stated in MPEP 2142, "the examiner bears the initial burden of factually supporting any *prima facie* conclusion of obviousness. If the examiner does not produce a *prima facie* case, the applicant is under no obligation to submit evidence of nonobviousness."²

Here, the Office relies on inherency to establish the presence of two claimed features in Kawabata et al. This requires a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art. *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990) (emphasis in original). The Office specifically relies on alleged similarity between the compositions and processes of Appellants and Kawabata et al. But evidence of record in this application establishes that the respective compositions and processes of Appellants and Kawabata et al. are not "substantially identical" per the standard of MPEP 2112 and *In re Best*; instead, they are substantially different.

In this case, the reasoning provided in the current rejection is limited to a statement that "the composition of the ferritic Cr-contained steel of Kawabata overlaps with the composition of the steel of the instant invention and ... the steel of Kawabata is made using a method similar to the method of the instant invention." The Office has not established *prima facie* obviousness and the burden has not shifted to Appellants to establish non-obviousness. Specifically, as set forth in the following subsections, the claimed and prior art products are not identical or substantially identical in structure or composition (they are instead substantially different), and they are not produced by identical or substantially identical processes. (they are instead produced using substantially different processes).

² Specifically, when relying upon MPEP 2112, "the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art." MPEP 2112(IV) (quoting *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990) (emphasis in original)).

a) THE RECORD SHOWS THAT THE CLAIMED AND PRIOR ART PRODUCTS ARE NOT IDENTICAL OR SUBSTANTIALLY IDENTICAL IN STRUCTURE OR COMPOSITION

The evidence of record in this application shows that the claimed and prior art products are not identical or substantially identical in structure or composition. Specifically, as noted below, Appellants' claimed steel and products of Kawabata et al. are not identical or substantially identical in structure or composition.

Appellants' claimed steel includes, among other features, the following specific steel composition:

- (1) W of about 2.05 to about 6.0% in percent by mass,
- (2) precipitated W of 0.005% to 0.1% in percent by mass, and
- (3) average thermal expansion coefficient between 20°C and 800°C less than about $12.6 \times 10^{-6}/^{\circ}\text{C}$.

Regarding their respective structures and compositions, steels of Appellants and Kawabata et al. differ at least with respect to their W and precipitated W contents. These differences are substantial.

First, Appellants' steel includes W of about 2.05 to about 6.0% in percent by mass as recited in claim 13. In contrast, the steel of Kawabata et al. may or may not optionally include any W. Specifically, Kawabata et al. discloses that "one or more elements selected from ... W: 0.1-5 wt% ... may further be included." Kawabata et al. at column 8, lines 37-44 (emphasis added). In fact, only one of the 101 samples of Kawabata et al. (sample 86) includes any W content, and that content (1.5 wt%) is outside Appellants' claimed range of about 2.05 to about 6.0% in percent by mass.

The significance of this difference in W content as between the steels of Appellants and Kawabata et al. is a matter of record in this application. For example, the Declaration of Yasushi Kato submitted with Appellants' Response of March 9, 2011 shows the impact of W content on the average thermal expansion coefficient, a claimed property of Appellants' steel product. Specifically, Fig. B of the Declaration includes data of precipitated W at $\leq 0.01\%$ and shows that when the amount of added

W is 2% or more, the average thermal expansion coefficient obtained is less than $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between 20°C and 800°C . Declaration of Yasushi Kato at page 2 (see Evidence Appendix). Fig. B also includes data showing that as added W decreases in amounts less than 2%, the average thermal expansion coefficient obtained increases above $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between 20°C and 800°C . Accordingly, evidence of record shows that this difference in W content as between the steels of Appellants and Kawabata et al. is a substantial difference at least in its established impact on Appellants' claimed average thermal expansion coefficient.

Second, Appellants' steel includes precipitated W of 0.005% to 0.1% in percent by mass as recited in claim 13. In contrast, the steel of Kawabata et al. is silent as to any precipitated W content. As noted previously, only one of the 101 samples of Kawabata et al. (sample 86) includes any W content without any indication of precipitated W. The remaining 100 samples have no W content and could not have any precipitated W content.

The significance of this difference in precipitated W content as between the steels of Appellants and Kawabata et al. is a matter of record in this application. For example, the Declaration of Yasushi Kato shows the impact of precipitated W content on the average thermal expansion coefficient. Specifically, Fig. C of that Declaration includes data of W equal to about 3% and shows that when the amount of precipitated W is 0.1% or less, the average thermal expansion coefficient obtained is less than $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between 20°C and 800°C . Declaration of Yasushi Kato at page 2. Fig. C also includes data showing that as precipitated W increases in amounts more than 0.1%, the average thermal expansion coefficient obtained increases above $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between 20°C and 800°C . Accordingly, evidence of record shows that this difference in precipitated W content as between the steels of Appellants and Kawabata et al. is a substantial difference at least in its established impact on Appellants' claimed average thermal expansion coefficient.

During the Interview conducted by telephone on August 16, 2011, and in connection with the processing conditions of Kawabata et al., the Examiners cited the specific example in column 14 of Kawabata et al. that discloses annealing in which

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selected cold rolled sheet samples 1-32, 66, 68, 70, 72-74 were heated at 1150°C. However, none of these samples include any W and therefore differ from Appellants' claimed steel at least in terms of W content and precipitated W %. As noted above and in the Declaration, this difference is substantial.

During the Interview, the Examiners also cited a selected cold rolled sheet sample 86, the sole steel sample of Kawabata et al. that contains any W (1.5 wt%). However, as noted previously, even that sample differs from Appellants' claimed steel at least in terms of W content (it is outside the claimed range of about 2.05 to about 6.0% in percent by mass). Additionally, the Declaration of Yasushi Kato establishes that sample 86 would fall outside Appellants' claim. See Declaration of Yasushi Kato at page 2 and Figure A, which shows the data for sample 86 of Kawabata et al. falling outside the scope of Appellants' claimed invention.

Accordingly, evidence of record in this application shows that Appellants' claimed steel and the steel product of Kawabata et al. are not identical or substantially identical in structure or composition. In fact, evidence of record shows that they differ substantially.

b) THE RECORD SHOWS THAT THE CLAIMED AND PRIOR ART PRODUCTS ARE NOT PRODUCED BY IDENTICAL OR SUBSTANTIALLY IDENTICAL PROCESSES

Evidence already of record in this application also shows that the claimed and prior art products are not produced by identical or substantially identical processes. Specifically, as noted below, Appellants' claimed steel and the steel of Kawabata et al. are produced by processes that are substantially different.

As background, Kawabata et al. includes a disclosure of general process conditions such as annealing conditions. See, for example, the following disclosure of Kawabata at column 6, line 60 - column 7, line 2:

"After such a cold rolling, annealing-pickling or bright annealing may be conducted according to the usual manner. ... According to the invention, production conditions other than those in the above steps are not particularly critical, and may be within usual manner. For example, it is favorable that the heating temperature of slab is 1000-1300 C, and the annealing temperature is 700-1300 C"

In contrast to this disclosure of general annealing conditions, Appellants discovered a steel product having particular characteristics that result from careful control of particular process conditions. These conditions include annealing within temperature ranges such as, for example, by hot-rolled-sheet annealing at 950 to 1150 C (more preferably 1020 to 1150 C) and by finish annealing at 1020 to 1200 C. Appellants' process is addressed in the following sub-sections in connection with Appellants' claimed precipitated W and Appellants' claimed average thermal expansion coefficient.

Precipitated W %

The respective processes of Appellants and Kawabata et al. differ at least with respect to the control of precipitated W %, which is influenced by W content control and annealing conditions. These differences are substantial. Appellants' claimed precipitated W % has been discovered to decrease the thermal expansion coefficient of alloys. For Example, Appellants' FIG. 4 shows the relationship between precipitated W and thermal fatigue life. See paragraph 0013 and also paragraphs 0003 and 0004 of Appellants' substitute specification (see Evidence Appendix).

The control of precipitated W % (including adding W and decreasing precipitated W) depends on several factors according to Appellants' disclosed process:

- Amount of W - simply adding W is not sufficient because a large amount of precipitated W actually increases the thermal expansion coefficient. Paragraph 0003 of Appellants' substitute specification (see Exhibit Appendix).
- Annealing conditions - FIG. 5 shows the influence of annealing temperatures on the amount of precipitated W. Paragraph 0014 of substitute specification.
 - Hot-rolled-sheet annealing temperature: preferably 950 to 1150 C, more preferably 1020 to 1150 C.
 - Finish annealing temperature: 1020 to 1200 C. Paragraph 0050 and paragraphs 0036, 0037 and 0046 of substitute specification (see Exhibit Appendix).

In contrast, the process of Kawabata et al. does not include any control of precipitated W % or specific control of annealing conditions. Accordingly, the claimed and prior art products are not produced by identical or substantially identical processes; in fact, they are instead substantially different. The significance of the differences between the Appellants' and prior art processes is explained throughout Appellants' specification, aspects of which are presented in the following paragraphs.

Regarding Appellants' control of precipitated W %, for example, Appellants found that addition of W to the Fe--Cr ferritic alloys and a decrease in the amount of precipitated W remarkably contributed to a decrease in thermal expansion coefficient of the alloys. Paragraph 0003 of Appellants' substitute specification. They discovered that simple addition of W is not sufficient, and a large amount of precipitated W rather increases the thermal expansion coefficient. Paragraph 0003. This is because when W is in a state of precipitated W, it inhibits a decrease in the thermal expansion coefficient. Paragraph 0003.

Appellants' Fig. 1 illustrates the influence of the amount of added W and the amount of precipitated W on an average thermal expansion coefficient. Paragraph 0010 of Appellants' substitute specification (see Exhibit Appendix). The Declaration of Yasushi Kato includes Fig. A, which comprises Appellants' Fig. 1 and specifically shows that the average thermal expansion coefficient is improved when the process is controlled in terms of added W content and precipitated W %.

Appellants' discovered that W is an extremely important element; specifically, because addition of W largely reduces thermal expansion coefficient, the amount of W was determined to be about 2.0% or more. Paragraph 0022 of Appellants' substitute specification (see Exhibit Appendix). In contrast, the process of Kawabata et al. only includes W as an optional component that may or may not be included. Additionally, Kawabata et al. is silent as to the control of precipitated W %.

Regarding Appellants' control of annealing conditions, Appellants discovered that it is important to determine the hot-rolled sheet annealing temperature and the finish annealing temperature to obtain precipitate W of 0.1% or less. Paragraph 0036 of Appellants' substitute specification (see Exhibit Appendix). Appellants' Fig. 5 illustrates the influence of the hot-rolled-sheet annealing temperature on the amount of precipitated W. Paragraph 0050 of the substitute specification. It specifically shows that an increase in the hot-rolled-sheet annealing temperature reduces the amount of precipitated W %, and a decrease in the hot-rolled-sheet annealing temperature increases the amount of precipitated W %. More specifically, a decrease in hot-rolled-sheet annealing temperature below about 950°C increases the amount of precipitated W % toward an amount above Appellants' claimed upper limit of 0.1%. Additionally, the impact of finish annealing temperature on precipitated W is set forth by Appellants in paragraphs 0036 and 0037 of the substitute specification (see Exhibit Appendix).

During the Interview, the Examiners cited the specific example in column 14 of Kawabata et al. that discloses annealing in which selected cold rolled sheet samples 1-32, 66, 68, 70, 72-74 were heated at 1150°C. As noted previously, none of these samples includes any addition of W in their process and therefore differ from Appellants' process at least in terms of the control of W content. Additionally, it is

noted that the selected cold rolled sheet samples 1-32, 66, 68, 70, 72-74 represent 38 of a total of 101 samples taught by Kawabata et al. Accordingly, the selected samples represent much less than half the samples of Kawabata et al., which expressly discloses general annealing conditions (namely, an annealing temperature of 700-1300 C). Accordingly, the general annealing conditions of Kawabata et al. differ significantly from Appellants' controlled annealing. This difference is substantial at least because of its established impact on Appellants' claimed precipitated W %.

For these reasons, Appellants' claimed steel and the steel of Kawabata et al. are produced by processes that are substantially different in terms of the control of W content and the control of annealing conditions. Evidence of these differences, and their impact on Appellants' claimed precipitated W, is found throughout Appellants' specification and figures as set forth above.

Thermal Expansion Coefficient

Benefits of the claimed thermal expansion coefficient include suitability for applications in which a heat cycle is repeated between high and low temperatures. Paragraph 0001 of the substitute specification (see Exhibit Appendix). The control of thermal expansion coefficient depends on several factors according to Appellants' disclosed process:

- FIG. 1 shows the influence of the amounts of added W and precipitated W on an average thermal expansion coefficient. Paragraph 0010 of the substitute specification.
- When the precipitated W exceeds 0.1%, the decrease in thermal expansion coefficient due to the addition of W is small. Finish annealing temperature must be increased significantly in order to restrain the precipitated W to be less than 0.005%, which results in extremely coarsened crystal grains, consequently orange peel occurs during working, cause a crack during working. Paragraphs 0023 and 0046 of the substitute specification.

Therefore, the record itself establishes that Appellants' claimed steel and the steel of Kawabata et al. are produced by processes that are not identical or substantially identical.

As noted above, Appellants' Fig. 1 illustrates the influence of the amount of added W and the amount of precipitated W on an average thermal expansion coefficient. For example, when the precipitated W exceeds 0.1%, the effect of decrease in thermal expansion coefficient due to addition of W is small; therefore, the upper limit of the amount of precipitated W was determined by Appellants to be about 0.1% or less. Paragraph 0023 of the substitute specification. As noted previously, the Declaration of Yasushi Kato includes Fig. A, which comprises Appellants' Fig. 1 and specifically shows that the average thermal expansion coefficient is improved when the process is controlled in terms of added W content and precipitated W %.

The significance of the difference in the control of W content as between the processes of Appellants and Kawabata et al. is a matter of record in this application. As noted previously, the Declaration of Yasushi Kato shows the impact of controlling W content on the average thermal expansion coefficient. Specifically, Fig. B includes data of precipitated W at $\leq 0.01\%$ and shows that when the amount of added W is controlled to be 2% or more, the average thermal expansion coefficient obtained is less than $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between 20°C and 800°C . Declaration of Yasushi Kato at page 2. Fig. B of the Declaration also includes data showing that as W is added in an amount that is less than 2%, the average thermal expansion coefficient obtained increases above $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between 20°C and 800°C . Accordingly, evidence of record shows that this difference in the control of W content as between the processes of Appellants and Kawabata et al. is a substantial difference.

The significance of the difference in the control of precipitated W content as between the processes of Appellants and Kawabata et al. is also a matter of record in this application. For example, the Declaration of Yasushi Kato shows the impact of controlling precipitated W content on the average thermal expansion coefficient. Specifically, Fig. C includes data of W equal to about 3% and shows that when the amount of precipitated W is controlled to be 0.1% or less, the average thermal expansion coefficient obtained is less than $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between

20°C and 800°C. Declaration of Yasushi Kato at page 2. Fig. C of the Declaration also includes data showing that as precipitated W is controlled to be increased in amounts more than 0.1%, the average thermal expansion coefficient obtained increases above $12.6 \times 10^{-6}/^{\circ}\text{C}$ at a temperature between 20°C and 800°C. Accordingly, evidence of record shows that this difference in the control of precipitated W content as between the steels of Appellants and Kawabata et al. is a substantial difference.

For these additional reasons, and in view of Appellants' control of W content, precipitated W content, and annealing conditions, Appellants' claimed steel and the steel of Kawabata et al. are produced by processes that are substantially different. As noted, precipitated W is influenced by Appellants' control of W content and the control of annealing conditions, which distinguish Appellants' process from that of Kawabata et al. Also, Appellants' claimed average thermal expansion coefficient is influenced by Appellants' control of precipitated W, which further distinguishes Appellants' process from that of Kawabata et al. Evidence of these differences, and their impact on Appellants' claimed precipitated W % and Appellants' claimed average thermal expansion coefficient, is found throughout Appellants' specification and figures and in the Declaration of Yasushi Kato as set forth above.

c) THE BURDEN TO ESTABLISH NON-OBVIOUSNESS HAS NOT SHIFTED TO APPELLANTS

Appellants respectfully submit that the burden has not shifted to Appellants because the Office failed to set forth a *prima facie* case of obviousness under the standard of MPEP § 2112. Accordingly, Appellants are under no obligation to submit evidence of nonobviousness.

As set forth above, the record establishes that the respective products and processes of Appellants and Kawabata et al. differ and do so substantially. This evidence far outweighs the conclusory statement in the rejection that "the steel of Kawabata is made using a method similar to the method of the instant invention." Office Action dated October 15, 2010, bridging pages 3 and 4.

Additionally, Appellants respectfully submit that the standard applied by the Office is incorrect. Appellants note that the Office concludes that "one of ordinary skill

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in the art would expect the steel of Kawabata to inherently have a similar amount of precipitated W and a similar average thermal expansion coefficient." Office Action dated October 15, 2010, bridging pages 3 and 4. This alleged "similarity" of precipitated W and average thermal expansion coefficient is not adequate to establish *prima facie* obviousness based on inherency under MPEP 2112. Inherent disclosure requires identity, not similarity.

Finally, the Office alleges that "the steel of Kawabata is made using a method similar to the method of the instant invention." Office Action dated October 15, 2010, bridging pages 3 and 4. This alleged "similarity" is also inadequate to establish *prima facie* obviousness based on inherency under MPEP 2112. Instead, there must be a basis in fact to conclude that the processes are "identical or substantially identical." Specifically, a *prima facie* case of obviousness under MPEP § 2112.01(I) can be made by reference to the compositions and processes of the prior art, but this requires that the claimed product and the prior art product are produced by identical or substantially identical processes. MPEP § 2112.01(I) states that "[w]here the claimed and prior art products are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a *prima facie* case of either anticipation or obviousness has been established." (citing *In re Best*, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977)).

As set forth above, the evidence of record in this application shows that both the respective products and processes of Kawabata et al. and Appellants differ substantially and in ways directly related to Appellants' claimed precipitated W % and Appellants' claimed average thermal expansion coefficient. Therefore, the respective products and processes cannot be said to be substantially identical. For these reasons, the evidence of record renders *prima facie* obviousness based on inherency under MPEP § 2112 improper.

III. ASSUMING ARGUENDO THAT THE OFFICE HAS ESTABLISHED PRIMA FACIE OBVIOUSNESS, APPELLANTS HAVE SUCCESSFULLY REBUTTED PRIMA FACIE OBVIOUSNESS BASED ON EVIDENCE OF RECORD IN THIS APPLICATION

In this Section, it is assumed *arguendo* that the Office had established *prima facie* obviousness. Appellants' do not admit that *prima facie* obviousness has been established and instead have shown that it has not been established. Nevertheless, in this Section Appellants demonstrate that, if made, a case of *prima facie* obviousness has been successfully rebutted based on the evidence of record in this application.

As noted previously, even if a *prima facie* case is established based on inherency, it can be rebutted by evidence showing that prior art products alleged to inherently disclose characteristics of a claimed product do not, in fact, necessarily possess the characteristics of the claimed product. Evidence of record in this application shows that the products of Kawabata et al. do not necessarily possess either of Appellants' claimed precipitated W % or Appellants' claimed average thermal expansion coefficient.

Specifically, MPEP § 2112 cited in the Office Action states that "[a] *prima facie* case can be rebutted by evidence showing that the prior art products do not necessarily possess the characteristics of the claimed product." (emphasis in original)(citing *In re Best*, 562 F.2d at 1255, 195 USPQ at 433 and *Titanium Metals Corp. v. Banner*, 778 F.2d 775, 227 USPQ 773 (Fed. Cir. 1985)). MPEP § 2112.01(I). Accordingly, *In re Best* and MPEP § 2112 provide the standard for rebutting a case of *prima facie* obviousness that is based on similarities between prior art and claimed products and processes to account for a characteristic that is not expressly disclosed in the prior art.

MPEP § 2112 relates to rejections based on inherency consistent with its title (Requirements of Rejection Based on Inherency; Burden of Proof), and *In re Best* is an inherency case. Whether or not a rejection specifically refers to inherency (as it does in this case), a rejection based on similarities between prior art and claimed products and processes (to account for a characteristic that is not expressly disclosed in the prior art) can therefore be rebutted under MPEP § 2112 by evidence showing that the

prior art products do not necessarily possess the characteristics of the claimed product.

The record itself shows that the prior art steel of Kawabata et al. does not necessarily possess the characteristics of the claimed product. More specifically, evidence of record demonstrates that the steel of Kawabata et al. does not necessarily possess Appellants' claimed precipitated W and Appellants' claimed average thermal expansion coefficient. It is especially clear that the steel product of Kawabata et al. does not necessarily possess the characteristics of Appellants' claimed product in view of the following evidence in the record of this application.

a) APPELLANTS' EXAMPLES ESTABLISH THAT THE STEEL OF KAWABATA ET AL. DOES NOT NECESSARILY POSSESS APPELLANTS' CLAIMED PRECIPITATED W AND AVERAGE THERMAL EXPANSION COEFFICIENT LIMITATIONS

Neither the precipitated W % nor the average thermal expansion coefficient claimed by Appellants are necessarily present in the steel product disclosed by Kawabata et al. In fact, Appellants' examples show that steel according to the disclosure of Kawabata et al. would not have Appellants' claimed precipitated W % and thermal expansion coefficient.

For example, Appellants' steel products C, D, E, O, P, Q, R, S, and T all have elemental compositions within the ranges and general processing conditions disclosed by Kawabata et al. Nevertheless, every one of those steel products falls outside Appellants' claimed precipitated W % and thermal expansion coefficient ranges.

Illustrative examples: For product C, for example, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (0.580) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges:

C	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		0.580	D	1010
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The same is true for steel products D, E, O, P, Q, R, S, and T:

- For product D, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (1.850) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.
- For product E, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (1.980) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.
- For product O, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (0.110) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.
- For product P, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (1.660) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.
- For product Q, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the

precipitated W % (1.490) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.

- For product R, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (1.700) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.
- For product S, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (1.790) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.
- For product T, Appellants' Table 1 shows that all elemental components are within the general ranges and general processing conditions of Kawabata et al. based on the ranges disclosed by Kawabata et al. Nevertheless, the precipitated W % (1.140) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) are outside Appellants' claimed ranges.

Accordingly, Appellants' examples show that steel according to the disclosure of Kawabata et al. would not necessarily have Appellants' claimed precipitated W % and thermal expansion coefficient. Additionally, with respect to Appellants' claimed precipitated W %, the evidence compels a conclusion that Appellants' claimed precipitated W does not necessarily follow from Kawabata et al. This is at least because many examples according to Kawabata et al. include no W and therefore no precipitated W. It is therefore error to conclude that Appellants' claimed precipitated W % would necessarily follow from Kawabata et al.

b) APPELLANTS' EXAMPLES ESTABLISH THAT THE STEEL OF KAWABATA ET AL. DOES NOT NECESSARILY POSSESS APPELLANTS' CLAIMED PRECIPITATED W AND AVERAGE THERMAL EXPANSION COEFFICIENT LIMITATIONS EVEN FOR VARIOUS STEELS HAVING THE SAME COMPOSITION

Neither the claimed precipitated W % nor thermal expansion coefficient claimed by Appellants are necessarily present in the steel product disclosed by Kawabata et al. even for various steels having the same composition as one another. In fact, Appellants' examples show that such steels would not necessarily have Appellants' claimed precipitated W % and thermal expansion coefficient.

For example, Appellants' steel products 1, 2 and B have the same composition, a composition within the ranges and general processing conditions of Kawabata et al. Nevertheless, steel product B is outside Appellants' claimed precipitated W% and thermal expansion coefficient ranges. See also steel products 3, 4, 5, C, D (C and D are outside Appellants' claimed ranges); steel products 6, 7, E (E is outside Appellants' claimed ranges); and steel products N and O (O is outside Appellants' claimed ranges).

Illustrative example: Products 1, 2 and B have the same elemental components, which are all within the ranges and general processing conditions of Kawabata et al. Nevertheless, the precipitated W % (1.540) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) for product B are outside Appellants' claimed ranges:

1	0.003	0.35	1.05	14.8	1.88	2.05	0.52	0.008	0.009	C
2	0.003	0.35	1.05	14.8	1.88	2.05	0.52	0.008	0.092	C
B	0.003	0.35	1.05	14.8	1.88	2.05	0.52	0.008	1.540	D

As noted above, the same is true for steel products steel products 3, 4, 5, C, D (C and D being outside Appellants' claimed ranges); steel products 6, 7, E (E being outside Appellants' claimed ranges); and steel products N and O (O being outside Appellants' claimed ranges):

- Products 3, 4, 5, C, and D have the same elemental components, which are all within the ranges and general processing conditions of Kawabata et al. Nevertheless, the precipitated W % (0.580) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) for product C are outside Appellants' claimed ranges, and the precipitated W % (1.850) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) for product D are outside Appellants' claimed ranges.
- Products 6, 7, and E have the same elemental components, which are all within the ranges and general processing conditions of Kawabata et al. Nevertheless, the precipitated W % (1.980) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) for product E are outside Appellants' claimed ranges.
- Products N and O have the same elemental components, which are all within the ranges and general processing conditions of Kawabata et al. Nevertheless, the precipitated W % (0.110) and thermal expansion coefficient (greater than $12.6 \times 10^{-6}/^{\circ}\text{C}$) for product O are outside Appellants' claimed ranges.

Therefore, even if Kawabata et al. explicitly disclosed a steel having the same composition as Appellants' examples, it still would not necessarily follow that the steel would have Appellants' claimed precipitated W % and thermal expansion coefficient. Accordingly, Appellants' examples show in this additional way that the steel of Kawabata et al. would not necessarily have Appellants' claimed precipitated W % and thermal expansion coefficient.

c) EXAMPLES OF KAWABATA ET AL. ESTABLISH THAT THE STEEL OF KAWABATA ET AL. DOES NOT NECESSARILY POSSESS APPELLANTS' CLAIMED W CONTENT AND PRECIPITATED W %

Additionally, steel sample nos. 1-85 and 87-101 of Kawabata et al. do not contain any W and therefore cannot possess Appellants' claimed precipitated W% of 0.005% to 0.1% in percent by mass. Also, steel sample no. 86, the only sample of Kawabata et al. containing W (1.5 wt%), does not contain Appellants' claimed W content.

For the foregoing reasons, the evidence of record (including the Kawabata et al. reference, Appellants' specification and figures, and the Declaration of Yasushi Kato) clearly establishes that the steel of Kawabata et al. does not necessarily possess (1) Appellants' claimed precipitated W of 0.005% to 0.1% in percent by mass, or (2) Appellants' claimed average thermal expansion coefficient between 20°C and 800°C less than about $12.6 \times 10^{-6}/^{\circ}\text{C}$. Accordingly, the evidence of record in this application successfully rebuts an obviousness rejection under the standard of *In re Best* as required by MPEP 2112.01(I), even assuming *arguendo* that *prima facie* obviousness has been established.

This evidence renders the rejection based on MPEP 2112 inappropriate and establishes that at least Appellants' claimed precipitated W % and Appellants' claimed average thermal expansion coefficient are not necessarily possessed in the steel of the Kawabata et al. reference. In other words, based on the evidence currently of record in this application, the rejection based on Kawabata et al. fails to establish *prima facie* obviousness and, even if it were to establish *prima facie* obviousness, the rejection has been rebutted.

Additionally, it is noted that whether a certain characteristic may be present in a reference is not sufficient to establish a case of *prima facie* obviousness under MPEP 2112.01(I). Instead, the missing characteristic must necessarily be present in the thing described in the reference. Specifically, MPEP § 2112(IV) states that:

- "The fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish the inherency of that result or characteristic" (citing *In re Rijckaert*, 9 F.3d 1531, 1534, 28 USPQ2d 1955, 1957 (Fed. Cir. 1993)).

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- "Inherency ... may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient." (citing *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999)).

Therefore, whether or not Appellants' claimed precipitated W % and Appellants' claimed average thermal expansion coefficient may hypothetically occur or be present in a product of Kawabata et al. is not sufficient to establish the inherency of those claimed features.

For the foregoing reasons, Appellants' claimed precipitated W % and Appellants' claimed average thermal expansion coefficient would not be expected in Kawabata et al., and withdrawal of the rejection is respectfully requested.

d) EVIDENCE OF RECORD IN THIS APPLICATION HAS NOT BEEN FULLY CONSIDERED BY THE OFFICE IN CONNECTION WITH THE INHERENCY-BASED REJECTION

The Office considered evidence of record in this application in connection with criticality in the context of unexpected results. See, for example, the Advisory Action dated September 21, 2011 ("the evidence cited by Applicant does not demonstrate either unexpected results or criticality") and the Office Action dated May 5, 2011 at page 3 ("Fig. A is not commensurate in scope with the instant claims and does not demonstrate the criticality of either the added W% or the precipitated W% by comparing, for example, a steel with 0.004% precipitated W to a steel with 0.005% precipitated W and a steel with 0.11% precipitated W to a steel with 0.1% precipitated W.").

In this Brief and in the Response dated September 2, 2011, however, Appellants rely on this evidence primarily to show (1) that *prima facie* obviousness based on inherency has not been established by the Office because the respective compositions and processes of Appellants and Kawabata et al. differ substantially and (2) that *prima facie* obviousness based on inherency (even if made) has been rebutted by evidence that steel according to the disclosure of Kawabata et al. does not necessarily possess Appellants' claimed precipitated W % or Appellants' claimed average thermal expansion coefficient. Appellants' evidence should now be considered in this regard.

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**C. REJECTION OF CLAIMS 13-17, 20 AND 21 AS UNPATENTABLE OVER
CLAIMS 1-8, 10-14, AND 16 OF U.S. PATENT NO. 7,806,993 IN VIEW OF
KAWABATA ET AL.**

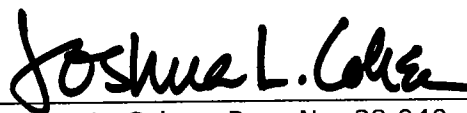
The rationale provided in connection with this rejection is the same as that provided in connection with the rejection under 35 U.S.C. § 103(a).

For at least those reasons set forth above in connection with the rejection under 35 U.S.C. § 103(a), this rejection should be reversed as well. In sum, the evidence of record cited above establishes that prior art products of Kawabata et al. would not necessarily possess Appellants' claimed precipitated W and Appellants' claimed average thermal expansion coefficient.

D. CONCLUSION

In view of the arguments set forth above, reversal of the rejections of the claims of the above-identified application is respectfully requested.

Respectfully submitted,



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Andrew J. Koopman, Reg. No. 65,537
Attorneys for Appellants

JLC/AJK/ap

Attachments: Claims Appendix
Evidence Appendix: Declaration of Yasushi Kato
Appellants' Substitute Specification and Figs. 1-5
Kawabata et al. U.S. Patent No. 5,626,694
Related Proceedings Appendix

Dated: February 6, 2012

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AJK_1386472

VIII. CLAIMS APPENDIX

1. – 12. (Cancelled)

13. (Previously Presented) A ferritic Cr-contained steel wherein a cold rolled annealed sheet is annealed, after cold rolling, at a final annealing temperature at 1050 to 1200°C, comprising C of about 0.03% or less, Mn of about 5.0% or less, Cr of about 6 to about 40%, N of about 0.03% or less, Si of about 5% or less, and W of about 2.05 to about 6.0% in percent by mass, and Fe and inevitable impurities as the remainder, wherein precipitated W is 0.005% to 0.1% in percent by mass, and an average thermal expansion coefficient between 20°C and 800°C is less than about $12.6 \times 10^{-6}/^{\circ}\text{C}$.

14. (Previously Presented) The ferritic Cr-contained steel according to Claim 13, further comprising at least one selected from the group consisting of Nb of about 1% or less, Ti of about 1% or less, Zr of about 1% or less, Al of about 1% or less, and V of about 1% or less in percent by mass.

15. (Previously Presented) The ferritic Cr-contained steel according to Claim 13 further comprising Mo of about 5.0% or less in percent by mass.

16. (Previously Presented) The ferritic Cr-contained steel according to Claim 13, further comprising at least one selected from the group consisting of Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less in percent by mass.

17. (Previously Presented) The ferritic Cr-contained steel according to Claim 13, further comprising at least one selected the group consisting of B of about

0.01% or less and Mg of about 0.01% or less in percent by mass.

18. (Withdrawn) The ferritic Cr-contained steel according to Claim 13, further comprising one or two of REM of about 0.1% or less and Ca of about 0.1% or less in percent by mass.

19. (Withdrawn) The ferritic Cr-contained steel according to Claim 14 further comprising Mo of about 5.0% or less in percent by mass.

20. (Previously Presented) The ferritic Cr-contained steel according to Claim 15, further comprising at least one selected from the group consisting of Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less in percent by mass.

21. (Previously Presented) The ferritic Cr-contained steel according to claim 13, further comprising at least one selected from the group consisting of Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less in percent by mass.

22. (Withdrawn) The ferritic Cr-contained steel according to Claim 14, further comprising at least one selected the group consisting of B of about 0.01% or less and Mg of about 0.01% or less in percent by mass.

23. (Withdrawn) A method of manufacturing ferritic Cr -contained steel comprising:

adjusting a composition of molten steel to include C of about 0.03% or less, Mn of about 5.0% or less, Cr of about 6 to about 40%, and N of about 0.03% or less, Si

of about 5% or less and W of about 2.0% to 6.0% in percent by mass, and Fe and inevitable impurities as the remainder;

forming the molten steel into a steel slab;

hot-rolling the slabs;

subjecting the hot-rolled-sheet to hot-rolled-sheet annealing at a hot-rolled-sheet annealing temperature of about 950 to 1150°C and descaling;

cold-rolling the hot rolled and annealed sheet;

and subjecting the cold-rolled-sheet to finish annealing at a finish annealing temperature of about 1020°C to about 1200°C, so that precipitated W is about 0.1% or less in percent by mass.

24. (Withdrawn) The manufacturing method according to Claim 23, wherein the composition of the molten steel further comprises at least one selected from the group consisting of Nb of about 1% or less, Ti of about 1% or less, Zr of about 1% or less, Al of about 1% or less, and V of about 1% or less in percent by mass.

25. (Withdrawn) The manufacturing method according to Claim 23, wherein the composition of the molten steel further comprises Mo of about 5.0% or less in percent by mass.

26. (Withdrawn) The manufacturing method according to Claim 23, wherein the composition of the molten steel further comprises at least one selected from the group consisting of Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less in percent by mass.

27. (Withdrawn) The manufacturing method according to Claim 23, wherein the composition of the molten steel further comprises at least one selected from the group consisting of B of about 0.01% or less and Mg of about 0.01% or less in percent by mass.

28. (Withdrawn) The manufacturing method according to Claim 23, wherein the composition of the molten steel further comprises one or two of REM of about 0.01% or less and Ca of about 0.1% or less in percent by mass.

29. (Withdrawn) The manufacturing method according to Claim 24, wherein the composition of the molten steel further comprises Mo of about 5.0% or less in percent by mass.

30. (Withdrawn) The manufacturing method according to Claim 24, wherein the composition of the molten steel further comprises at least one selected from the group consisting of Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less in percent by mass.

31. (Withdrawn) The manufacturing method according to Claim 25, wherein the composition of the molten steel further comprises at least one selected from the group consisting of Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less in percent by mass.

32. (Withdrawn) The manufacturing method according to Claim 24, wherein the composition of the molten steel further comprises at least one selected from the group consisting of B of about 0.01% or less and Mg of about 0.01% or less in percent by mass.

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33. (Withdrawn) The ferritic Cr-contained steel according to Claim 19, further comprising at least one selected from the group consisting of Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less in percent by mass.

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IX. EVIDENCE APPENDIX

Declaration of Yasushi Kato dated March 7, 2011 (submitted with Appellants' Response of March 9, 2011), a copy of which is annexed to this Brief. This evidence was entered in the record as noted on pages 3 and 7, for example, of the Office Action dated May 5, 2011.

Appellants' substitute specification filed June 16, 2006 ("SUBSTITUTE SPECIFICATION (Clean)") with Figures 1-5.

Kawabata U.S. Patent No. 5,626,694.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Art Unit	: 1733	Customer No. 035811
Examiner	: Caitlin Anne Fogarty	
Serial No.	: 10/583,220	Docket No.: JFE-06-1129
Filed	: June 16, 2006	
Inventors	: Atsushi Miyazaki	Confirmation No.: 7655
	: Yasushi Kato	
	: Osamu Furukimi	
Title	: FERRITIC Cr-CONTAINED STEEL	

DECLARATION OF YASUSHI KATO

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Yasushi Kato, am a citizen of Japan with an address at c/o JFE Steel Corporation, Steel Research Laboratories, Stainless Steel Research Department, 2-2-3 Uchisaiwaicho, Chiyodaku, Tokyo, 100-0011, Japan.

I hereby declare as follows:

April 1979	Entered Department of Iron & Steel Metallurgy, School of Engineering Kyushu University
March 1984	Graduated from the same. Received Bachelor of Engineering.
April 1984	Proceeded to Master's Program in Engineering Research, Kyushu University (Majored in Iron & Steel Metallurgy)
March 1986	Graduated from the same. Received Master's degree of Engineering.
April 1986	Entered Stainless Steel Research Laboratories, Research Laboratories, Kawasaki Steel Corporation
July 1992	Sent to study at Institute for Materials Research, Tohoku University
October 1994	Returned to Stainless Steel Research Laboratories, Research Laboratories, Kawasaki Steel Corporation
April 2003	Stainless Steel Research Laboratories, Steel Research Laboratories, JFE Steel Corporation (Merged company of Kawasaki Steel Corporation and NKK Corporation)
October 2007	Studied as a transfer student (last half term of a Doctor course for working people) of Doctor's degree of Material Process and Engineering of Graduate School of Kyushu University

April 2010	General Manager of Stainless Steel Research Laboratories, JFE Steel Corporation
September 2010	Finished Doctor's degree of Material Process and Engineering of Graduate School of Kyushu University. Received Doctor's degree of Engineering.
To present	(Working as mentioned above as the General Manager of Stainless Steel Research Laboratories, JFE Steel Corporation)

Attached to this Declaration are Figs. A, B and C. Those Figs. A-C are exactly the same as Figs. A-C attached to the Response that was filed in the United States Patent and Trademark Office on August 25, 2010.

I personally prepared those figures. Fig. A comprises Fig. 1 taken from the above-identified application to which data of examples in the specification was further added. Also, an example from US Patent No. 5,626,694 to Kawabata was taken from that publication. That example is example No. 86 from Table 4.

Fig. B is similar to Fig. A and includes data of precipitated W at $\leq 0.01\%$ and shows that when the amount of added W is 2% or more, the average thermal expansion coefficient obtained is less than 12.6×10^{-6} at a temperature between 20°C and 800°C . Fig. C is also similar to Fig. A and includes data wherein W is equal to about 3% and shows that when the amount of precipitated W is 0.1% or less, the obtained average thermal expansion coefficient is less than 12.6×10^{-6} at a temperature between 20°C and 800°C .

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: March 7 2011

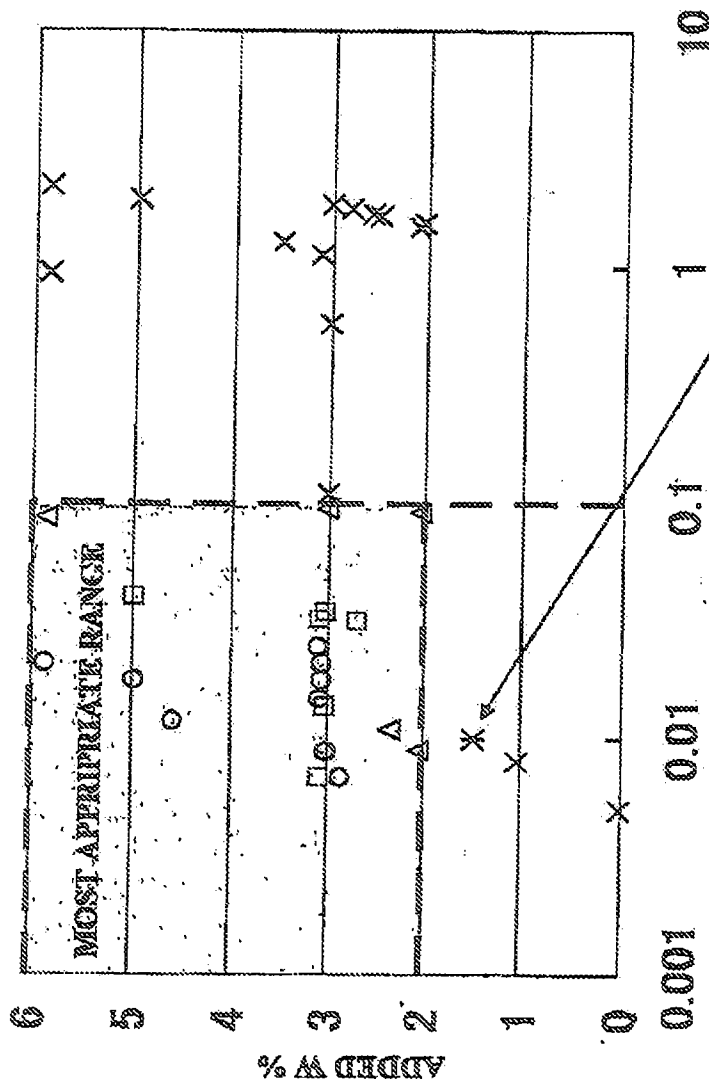
Yasushi Kato
Yasushi Kato, co-inventor

FOR DEMONSTRATION PURPOSES

O: RANK A, LESS THAN 11.7
 □: RANK B, 11.7 TO LESS THAN 12.1
 Δ: RANK C, 12.1 TO LESS THAN 12.6
 x: RANK D, 12.6 OR MORE
 *: KAWABATA PATENT

ATTACHED FIG. A

ADDED W AND
 PRECIPITATED W

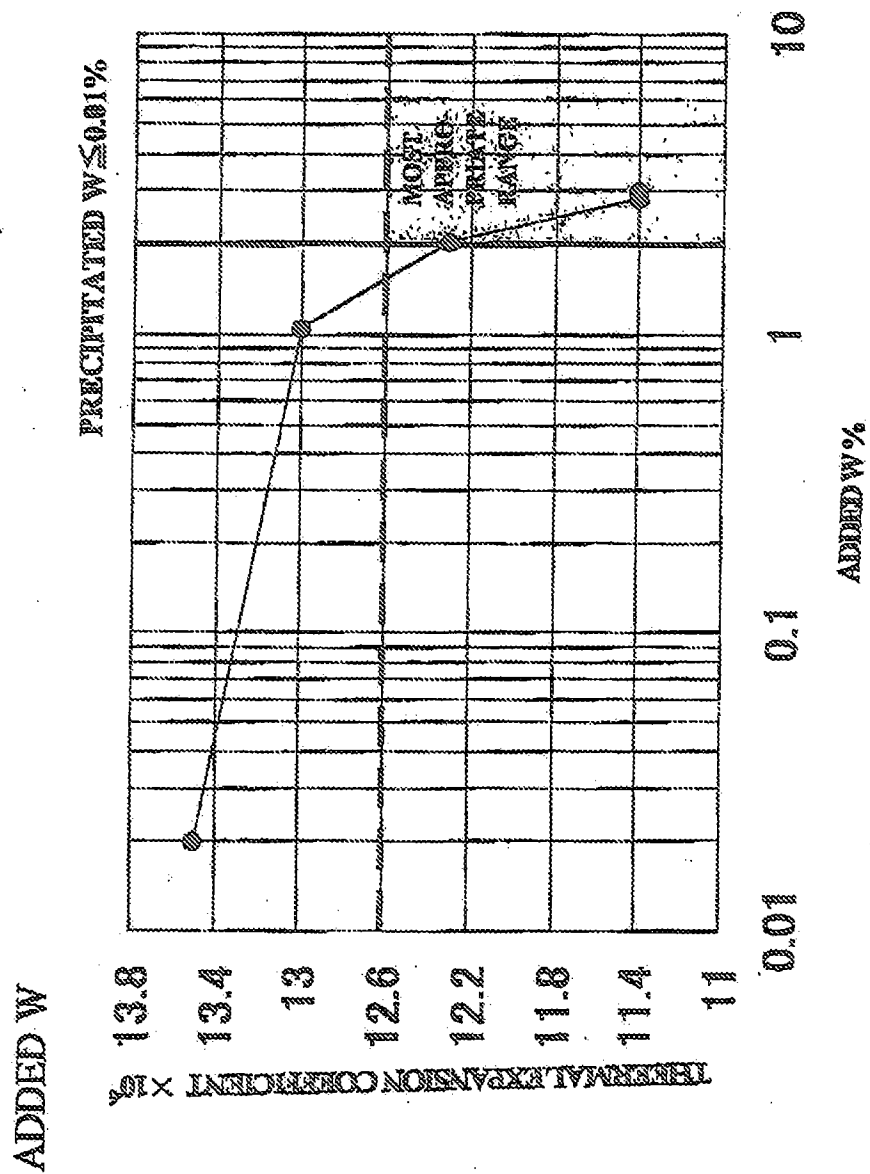


PRECIPITATED W %

KAWABATA PATENT
 (PRECIPITATED W=NOT INCLUDED
 IN MOST APPROPRIATE RANGE
 EVEN WHEN 0.01)

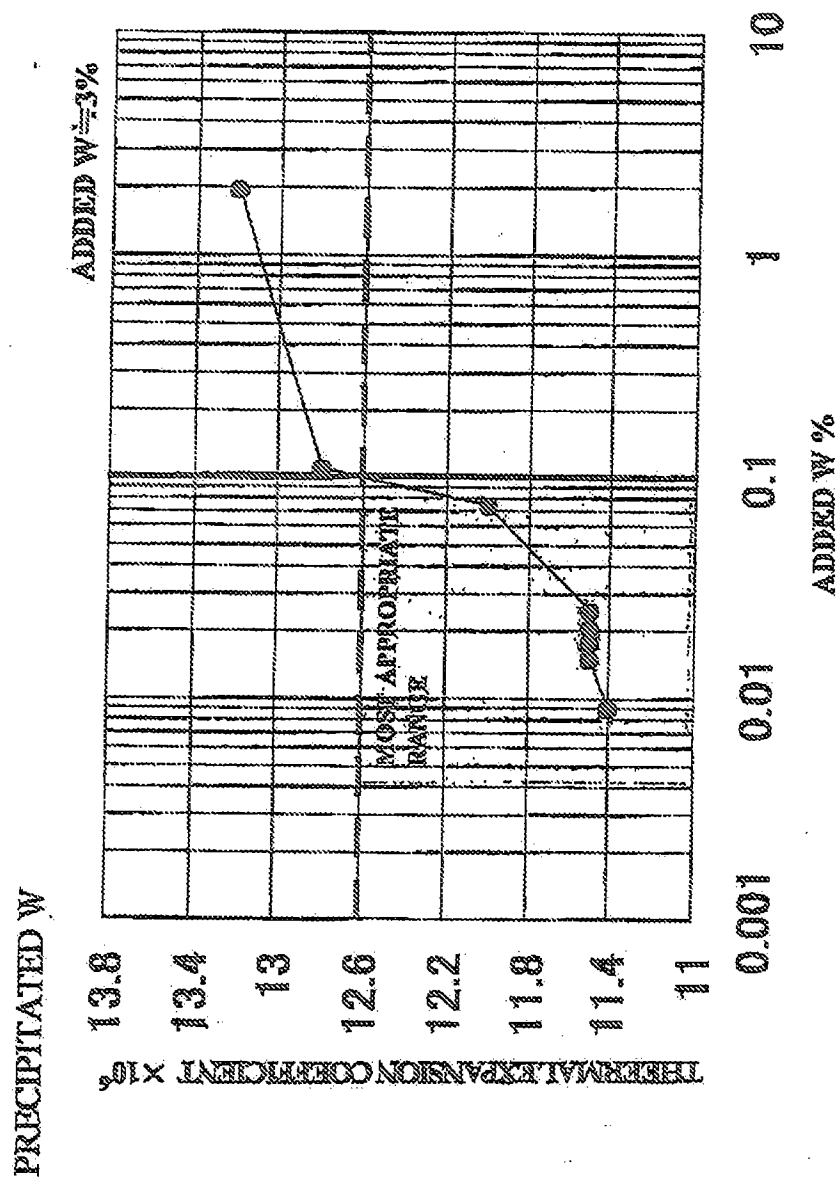
FOR DEMONSTRATION PURPOSES

ATTACHED FIG. B



FOR DEMONSTRATION PURPOSES

ATTACHED FIG. C



SUBSTITUTE SPECIFICATION (Clean)**Description****Ferritic Cr-Contained Steel****Technical Field**

[0001] The invention relates to ferritic Cr-contained steel having a low thermal expansion coefficient. This disclosure also relates to ferritic Cr-contained steel having a low thermal expansion coefficient suitable for applications in which a heat cycle is repeated between high temperature and low temperature, including exhaust system members of an automobile such as exhaust manifolds, exhaust pipes, converter case materials, and metal honeycomb materials; separators within a solid-oxide-type fuel cell; materials for interconnectors; materials for reformers as peripheral members of fuel cells; exhaust ducts of power generation plants; or heat exchangers. The thermal expansion coefficients described herein are linear expansion coefficient coefficients. It will hereinafter be abbreviated as thermal expansion coefficient.

Background

[0002] In various members subjected to the repeated heat cycle between high temperature and low temperature, heat expansion and contraction are repeated, as a result both of the members themselves and peripheral members of them are added with strain or stress, and consequently fracture by thermal fatigue is prone to occur. In such a circumstance, the fracture by thermal fatigue is hardly to occur in an alloy having a lower thermal expansion coefficient, because heat strain and heat stress to be added become smaller. As a known method for decreasing the thermal expansion coefficient, use of Magneto-volume effects is given. This is a method for decreasing the thermal expansion coefficient in such a way that when temperature is decreased, strain corresponding to a level of essentially contracted strain is compensated by magnetostriction due to generation of Atomic magnetic momentum or change in amount of the momentum. To obtain such magneto-volume effects, temperature dependence of the generation

or the change in amount of the atomic magnetic-momentum is important. For example, in Fe-36% Ni Invar alloy used for a shadow mask in a cathode ray tube of a display, since the amount of the Atomic magnetic momentum suddenly changes near the Curie temperature (230 to 279°C), a sudden decrease in thermal expansion coefficient is exhibited at a temperature lower than the Curie temperature (a value of thermal expansion coefficient of the alloy at about 200°C, at which the alloy is used for the shadow mask, is extremely low, about $1 \times 10^{-6} / ^\circ\text{C}$.) However, the alloy has an extremely high thermal expansion coefficient of about $18 \times 10^{-6} / ^\circ\text{C}$ at 800°C, which is in at the same level as in a typical austenitic stainless steel. Furthermore, the alloy contains Ni as much as 36%, resulting in an extreme increase in cost, consequently it is hard to be used for such an application in general consumer goods. From such reasons, Fe-Cr base alloys are widely used for the application. However, the Fe-Cr base alloys have a small temperature dependence of amount of the Atomic magnetic momentum is small, therefore the Magneto-volume effect is not observed even at a temperature of the Curie temperature or lower. In this way, decrease in thermal expansion coefficient due to Magneto-volume effect is difficult in the Fe-Cr base alloys. Therefore, in the related art, thermal fatigue life has been improved by a method using improvement in strength or high ductility by forming a high alloy (JP-A-2003-213377 and JP-A-2002-212685). However, improved strength by forming the high alloy necessarily causes a problem of reduction in workability, and orientation of high ductility causes strength to be extremely lowered, consequently it is pointed that another problem (for example, fatigue at elevated temperature) may occur. From such a situation, a new method has been strongly required for improving the thermal fatigue life by reducing the thermal expansion coefficient of Fe-Cr ferritic alloys.

Summary

[0003] We found that addition of W to the Fe-Cr ferritic alloys and a decrease in the amount of precipitated W remarkably contributed to a decrease in thermal expansion coefficient of the alloys. While a the mechanism of this has not been clarified, since it is known that the thermal expansion coefficient of the alloys also depends on specific heat and bulk modulus, it is believed that addition of W has an effect on the coefficient through the temperature dependence of the amount of the Atomic magnetic momentum. An especially important point is that simple

addition of W is not sufficient, and large amount of precipitated W rather increases the thermal expansion coefficient. The precipitated state of W is a precipitated state mainly in a form of the Laves phase (Fe_2M -type intermetallic compounds) or carbides, and when W is in a state of precipitated W, it inhibits a decrease in the thermal expansion coefficient. While the reason for this is not clear, we believe it is because of the following two points. The first point is considered as follows: while grain boundaries essentially act as a cushion for thermal expansion, since the Laves phase is precipitated therein, the cushion effect is reduced, and consequently the thermal expansion coefficient is increased.

[0004] The second point is considered as follows: when the amount of the precipitated W is increased in the alloy, the amount of solid soluted W is decreased, and consequently a decrease in the thermal expansion coefficient of the alloy is inhibited. However, even if the amount of precipitated W is slight, for example, only more than 0.1%, the decrease in thermal expansion coefficient of the alloy is inhibited, therefore the reason can not be explained only from the increase in the amount of dissolved W in the alloy. Thus, the former reason, a decrease in effect as a cushion of the grain boundaries is considered to be major. Therefore, component design of a material suitable for the environment in which heat cycle is applied can be realized by considering the knowledge on thermal expansion coefficient in addition to knowledge in the related art, that is, influence of various additional-elements on other properties such as workability, oxidation resistance, and corrosion resistance.

[0005] Select aspects of the disclosure include:

1. Ferritic Cr-contained steel containing C of 0.03% or less, Mn of 5.0% or less, Cr of 6 to 40%, N of 0.03% or less, Si of 5% or less, and W of 2.0% to 6.0% in percent by mass, and Fe and inevitable impurities as the remainder, wherein precipitated W is 0.1% or less in percent by mass, and an average thermal expansion coefficient between 20°C and 800°C is less than $12.6 \times 10^{-6}/^\circ\text{C}$.
2. The ferritic Cr-contained steel according to 1, further containing at least one selected from a group of Nb of 1% or less, Ti of 1% or less, Zr of 1% or less, Al of 1% or less, and V of 1% or less in percent by mass.

3. The ferritic Cr-contained steel according to 1 or 2, further containing Mo of 5.0% or less in percent by mass.
4. The ferritic Cr-contained steel according to any one of 1 to 3, further containing at least one selected from a group of Ni of 2.0% or less, Cu of 3.0% or less, and Co of 1.0% or less in percent by mass.
5. The ferritic Cr-contained steel according to any one of 1 to 4, further containing at least one selected from a group of B of 0.01% or less and Mg of 0.01% or less in percent by mass.
6. The ferritic Cr-contained steel according to any one of 1 to 5, further containing one or two of REM of 0.1% or less and Ca of 0.1% or less in percent by mass.
7. A manufacturing method of ferritic Cr-contained steel, wherein a composition of molten steel is adjusted to include C of 0.03% or less, Mn of 5.0% or less, Cr of 6 to 40%, N of 0.03% or less, Si of 5% or less, and W of 2.0% to 6.0% in percent by mass, and Fe and inevitable impurities as the remainder; and then the molten steel is formed into a steel slab; and then the slab is hot-rolled and then subjected to hot-rolled-sheet annealing at a hot-rolled-sheet annealing temperature of 950 to 1150°C and descaling; and furthermore, a hot rolled and annealed sheet is cold-rolled and then subjected to finish annealing at a finish annealing temperature of 1020°C to 1200°C, so that precipitated W is 0.1% or less in percent by mass.
8. The manufacturing method of ferritic Cr-contained steel according to 7, wherein the composition of the molten steel further includes at least one selected from a group of Nb of 1% or less, Ti of 1% or less, Zr of 1% or less, Al of 1% or less, and V of 1% or less in percent by mass.
9. The manufacturing method of ferritic Cr-contained steel according to 7 or 8, wherein the composition of the molten steel further includes Mo of 5.0% or less in percent by mass.
10. The manufacturing method of ferritic Cr-contained steel according to 7 to 9, wherein the composition of the molten steel further includes at least one selected from a group of Ni of 2.0% or less, Cu of 3.0% or less, and Co of 1.0% or less in percent by mass.
11. The manufacturing method of ferritic Cr-contained steel according to 7 to 10, wherein the composition of the molten steel further includes at least one selected from a group of B of 0.01% or less and Mg of 0.01% or less in percent by mass.

12. The manufacturing method of ferritic Cr-contained steel according to 7 to 11, wherein the composition of the molten steel further includes one or two of REM of 0.1% or less and Ca of 0.1% or less in percent by mass.

[0006] While the amount of "precipitated W" means mass percent of W precipitated mainly in a form of the Laves phase or carbides, mass percent of W precipitated in a form of another phase is also included. The mass percent of "precipitated W" was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). That is, a sample is electrolyzed at a constant current (current density $\leq 20 \text{ mA/cm}^2$) using a 10% acetylacetone-base electrolyte (commonly called AA solution). Electrolysis residue in the electrolytic solution is collected by filtration, then fused in alkali (sodium peroxide and metaboric lithium), and then dissolved in an acid and then diluted into a certain quantity by water. The solution is subjected to measurement of the amount of W (W_p) in the solution using an ICP emission spectrometer (Inductively Coupled Plasma Spectrometer). The amount of precipitated W (mass percent) can be obtained by the following formula:

$$\text{the amount of precipitated W (mass percent)} = (W_p / \text{sample weight}) \times 100.$$

[0007] The thermal expansion coefficient has temperature dependence even if a ferrite structure is remained as it is. Thus, average thermal expansion coefficient in use a real world environment is practically important. Therefore, we defined an average thermal expansion coefficient between 20°C and 800°C. The average thermal expansion coefficient between 20°C and 800°C described herein means a value of an elongation ratio in one direction of a steel sheet in the case of heating the steel sheet to 20°C to 800°C which is divided by temperature difference 780°C between 20°C and 800°C. However, since the Cr-contained steels effectively acts on decrease in thermal expansion coefficient even out of the temperature range, it will be appreciated that the limitation of the temperature range is not intended to limit the temperature in use a real world environment to the range of 20°C to 800°C.

[0008] Ferritic Cr-contained steel having a low thermal expansion coefficient compared with ferritic Cr-contained steel in the related art can be obtained. Thermal fatigue life at 100 to 800°C of such a material having a low thermal expansion coefficient exhibits an excellent value

compared with steels in the related art (ferritic stainless steel, Type 429Nb (JIS G4307) and ferritic heat-resistant steel, sheet SUH409L (JIS G4312)).

[0009] Therefore, the steel is used in a region to which heat cycle is applied, thereby thermal stress to the peripheral member and the steel itself is reduced, and therefore a problem in design for improving the life, or complicated design for reducing the thermal strain is not necessary. Therefore, the steels can be preferably used for applications of components to which heat cycle is applied, including the exhaust system components of the automobile, separators within the fuel cell, materials for interconnectors, materials for reformers, exhaust ducts of the power generation plants, or heat exchangers.

Brief Description of the Drawings

[0010] Fig. 1 is a diagram showing influence of the amount of added W and the amount of precipitated W on an average thermal expansion coefficient between 20 and 800°C of ferritic Cr-contained steel having a basic composition of 15% Cr-0.5% Nb-1.9% Mo;

[0011] Fig. 2 is a view of a test piece for thermal fatigue test (unit of numeral values is mm);

[0012] Fig. 3 is views showing heat cycle and restraining conditions, wherein thermal fatigue life was evaluated in a way that assuming that minimum temperature was 100°C and maximum temperature was 900°C as a heat cycle condition, and strain was zero at 500°C (intermediate temperature between 100°C and 900°C), and strain due to free thermal expansion was controlled such that a restraint ratio was 0.35;

[0013] Fig. 4 is a diagram showing a relation between the amount of precipitated W and the thermal fatigue life of the ferritic Cr-contained steel having the basic composition of 15% Cr-0.5% Nb-1.9% Mo; and

[0014] Fig. 5 is a diagram showing influence of hot-rolled-sheet annealing temperature on the amount of precipitated W of a cold rolled and annealed steel sheet of the ferritic Cr-contained steel having the basic composition of 15% Cr-0.5% Nb-1.9% Mo.

Detailed Description

[0015] Hereinafter, the reason for selecting elements to be in the composition within the above range is described. In the description, representation in “%” is representation in mass percent unless otherwise specified.

•C: 0.03% or less

[0016] Since C deteriorates toughness and workability, incorporation of C is preferably reduced at maximum. From the point, the amount of C was limited to about 0.03% or less in the invention. Preferably, the amount is about 0.008% or less.

•Mn: 5.0% or less

[0017] Mn is added for improving toughness. To obtain the effect, the amount of Mn of 0.1% or more is preferable. However, since excessive addition of Mn may cause formation of MnS, which deteriorates corrosion resistance, the amount was limited to about 5.0% or less. Preferably the amount is about 0.1% to about 5.0%, and more preferably about 0.5% to about 1.5%.

•Cr: 6 to 40%

[0018] Cr is also effective for improving corrosion resistance and oxidation resistance. Since W of 2.0% or more is added, if Cr of 6% or more exists in steel, the steel can be used for many applications from a point of corrosion resistance or oxidation resistance. In particular, when high-temperature oxidation resistance is regarded as important, Cr of 14% or more is preferably contained. When the amount of Cr exceeds 40%, embrittlement in material becomes significant; therefore the amount was determined to be about 40% or less. When workability is regarded as important, the amount of Cr is preferably less than about 20%, and more preferably less than about 17%.

[0019] Moreover, Cr is effective for decrease in thermal expansion coefficient, and in the light of this point, the amount of about 14% or more is preferable.

•N: 0.03% or less

[0020] Since N deteriorates toughness and workability similarly as C, incorporation of N is preferably reduced at maximum. From this point, the amount of N was limited to about 0.03% or less. More preferably, the amount is about 0.008% or less.

•Si: 5% or less

[0021] Si is added for improving oxidation resistance. To obtain the effect, the amount of Si is preferably 0.05% or more. When the amount exceeds 5%, strength at room temperature is increased, which deteriorates workability, therefore the upper limit of the amount was determined to be about 5%. Preferably, the amount is about 0.05% to about 2.00%.

•W: 2.0% to 6.0%

[0022] W is an extremely important element. Since addition of W largely reduces thermal expansion coefficient, the amount of W was determined to be about 2.0% or more. However, when the amount is excessively increased, strength at room temperature is increased, which deteriorates workability, therefore the upper limit of the amount was determined to be about 6.0%. Preferably, the amount is about 2.5% to about 4%, and more preferably about 3% to about 4%.

•Precipitated W: 0.1% or less

[0023] The precipitated W is precipitated mainly in the form of the Laves phase or carbides. When the precipitated W exceeds 0.1%, the effect of decrease in thermal expansion coefficient due to addition of W is small. Therefore, the upper limit of the amount of precipitated W was determined to be about 0.1% or less. Preferably, the amount is about 0.05% or less, and more preferably about 0.03% or less. The lower amount is more preferable. However, finish annealing temperature must be increased significantly in order to restrain the precipitated W to be less than 0.005%, which results in extremely coarsened crystal grains, consequently orange peel occurs during working, cause a crack during working. Therefore, particularly when the steel of the application is used for an application requiring working, it is more preferable that the amount of precipitated W is substantially about 0.005% or more. While the amount of "precipitated W" means mass percent of W precipitated mainly in the form of the Laves phase or carbides, it may include mass percent of W precipitated in a form of another

phase. In measurement of the mass percent of "precipitated W", the electrolysis residue was measured in the inductively coupled plasma atomic emission spectrometry as described before.

[0024] Hereinbefore, while basic components have been described, in addition to this, the following elements can be appropriately contained as necessary in the invention.

- At least one selected from Nb of about 1% or less, Ti of about 1% or less, Zr of about 1% or less, Al of about 1% or less, and V of about 1% or less

[0025] Any of Nb, Ti, Zr, Al and V acts to fix C or N and thus improves intergranular corrosion resistance, and from this point, each of them is preferably contained about 0.02% or more. However, when the amount exceeds 1%, embrittlement of steel is caused; therefore they are determined to be contained about 1% or less respectively.

- Mo: 5.0% or less

[0026] Mo may be added because it improves corrosion resistance. While the effect appears at the amount of about 0.02% or more, excessive addition of Mo deteriorates workability, therefore the amount of about 5.0% was determined as the upper limit. The amount is preferably about 1% to about 2.5%.

- At least one selected from Ni of 2.0% or less, Cu of 3.0% or less, and Co of 1.0% or less

[0027] Any of Ni, Cu, and Co is a useful element for improving toughness, and Ni of about 2.0% or less, Cu of about 3.0% or less, and Co of about 1.0% or less were determined to be contained respectively. Ni of about 0.5% or more, Cu of about 0.3% or more, and Co of about 0.01% or more are preferably added so that effects of the elements are sufficiently exhibited.

- At least one selected from B of 0.01% or less and Mg of 0.01% or less

[0028] Both of B and Mg effectively contribute to improvement in secondary embrittlement. To obtain the effect, B of about 0.0003% or more and Mg of about 0.0003% or more are preferable respectively. However, in each of B and Mg, when the amount exceeds 0.01%, strength at room temperature is increased, causing deterioration in ductility, therefore

they are determined to be contained about 0.01% or less respectively. More preferably, B is about 0.002% or less, and Mg is about 0.002% or less.

•At least one REM of 0.1% or less and Ca of 0.1% or less

[0029] REM and Ca effectively contribute to improvement in oxidation resistance. To obtain the effect, REM of about 0.002% or more and Ca of about 0.002% or more are preferable respectively. However, since excessive addition of them deteriorates corrosion resistance, they are determined to be contained about 0.1% or less respectively. In the invention, REM means lanthanoid series elements and Y. In particular, when Ti is contained, Ca effectively contributes also to prevention of nozzle clogging during continuous casting. The effect becomes significant at the Ca amount of about 0.001% or more.

[0030] Next, a microstructure of a steel sheet is described. A structure of steel manufactured using a technique of the application is substantially a ferrite single phase. While the steel may have a structure partially containing bainite, in a condition that cooling has been performed after hot rolling and coiling, steel after cold rolling and annealing substantially has the structure of the ferrite single phase. In the steel of the application, component design is made such that hard martensite is not formed in a condition before working such as cold rolling and annealing.

[0031] Next, a preferred manufacturing method of the steel is described. Manufacturing conditions of the steel is not particularly limited except that the hot-rolled sheet annealing temperature and the finish annealing temperature are determined to obtain precipitated W of 0.1% or less, and a typical manufacturing method of the ferritic stainless steel can be preferably used.

[0032] For example, molten steel that has been adjusted in the appropriate composition range is ingoted using an ingot furnace such as a converter and an electric furnace, or using refining such as ladle refining and vacuum refining, and then an ingot is formed into a slab by an ingot casting-blooming method, and then the slab is hot-rolled. Furthermore, a hot-rolled and annealed sheet is subjected to hot-rolled sheet annealing in which temperature is controlled to be in a predetermined temperature range, and then subjected to pickling. Furthermore, a hot-rolled

sheet is subjected to cold rolling, and then a cold-rolled and annealed sheet is subjected to finish annealing in which temperature is controlled to be in a predetermined temperature range, and subjected to pickling. A cold rolled and annealed sheet is preferably formed sequentially through the above process.

[0033] In a more preferable manufacturing method, part of conditions of a hot rolling process and a cold rolling process are made to be specific conditions. In steel making, it is preferable that molten steel containing the essential components and components added as necessary is ingoted in the converter or the electric furnace, and then an ingot is subjected to secondary refining by a VOD method. While the molten steel formed into the ingot can be formed into a steel material according to a known manufacturing method, continuous casting is preferably used in the light of productivity and quality. A steel material obtained by the continuous casting is heated, for example, to about 1000 to about 1250°C, and then formed into a hot-rolled sheet having a desired thickness. Naturally, the material can be worked into other forms than a sheet material. The hot-rolled sheet is subjected to batch annealing or continuous annealing at about 950 to about 1150°C, and more preferably about 1020 to about 1150°C, and then descaled by pickling and the like to be formed into a hot-rolled sheet product. Shot blasting may be performed for descaling before pickling as necessary.

[0034] Furthermore, the obtained hot rolled and annealed sheet is formed into a cold-rolled sheet through the cold rolling process. In the cold rolling process, at least two steps of cold rolling including intermediate annealing may be performed as necessary for production reasons. Total reduction rate during the cold rolling process including one or at least two steps of cold rolling is made to be about 60% or more, preferably about 62% or more, and more preferably about 70% or more. A cold rolled sheet is subjected to continuous annealing (finish annealing) at about 1020°C to about 1200°C and more preferably about 1050°C to about 1150°C, and then subjected to pickling to be formed into a cold rolled and annealed sheet. In some applications, light rolling (for example, skin-pass rolling) can be applied after cold rolling and annealing to adjust a shape of the steel sheet or quality.

[0035] A cold rolled and annealed sheet product manufactured in this way is used to form exhaust pipes of the automobile or a motorcycle, an outer casing material of a catalyst and

exhaust duct of a thermal power plant, the heat exchanger, or fuel-cell-related members (including the separator, interconnector, and reformer) by performing bending and the like to the product depending on respective applications. A welding method for welding the members is not particularly limited, and typical arc welding methods such as MIG (Metal Inert Gas), MAG (Metal Active Gas) and TIG (Tungsten Inert Gas), laser welding, resistance welding methods such as spot welding and seam welding, high-frequency resistance welding such as a electric resistance welding, and high frequency induction welding can be used.

[0036] Particularly, it is important to determine the hot-rolled sheet annealing temperature and the finish annealing temperature to obtain precipitate W of 0.1% or less.

(1) Hot-rolled-sheet annealing temperature: 950°C to 1150°C, and finish annealing temperature: 1020°C to 1200°C.

[0037] When temperature of hot-rolled-sheet annealing is less than 950°C, large amount of precipitated W is remained in steel; therefore unless temperature of subsequent finish annealing exceeds 1200°C, the amount of precipitated W of cold rolled and annealed sheet does not satisfy $W \leq 0.1\%$. However, when the finish annealing temperature is set to be more than 1200°C, a finish-annealed structure is significantly coarsened, causing orange peel. On the other hand, when the hot-rolled-sheet annealing temperature is more than 1150°C, a hot rolled and annealed structure having coarse crystal grains is formed, and consequently toughness of the hot rolled sheet is deteriorated, which causes break of a coil during cold rolling. Accordingly, the hot-rolled-sheet annealing temperature is preferably 950 to 1150°C, and more preferably 1020°C to 1150°C. The finish annealing temperature is set to be 1020°C to 1200°C, and more preferably 1050°C to 1150°C under such a hot-rolled-sheet annealing temperature condition, thereby precipitated W of 0.1% or less can be obtained.

Example 1

[0038] 50 kg steel ingots having compositions as shown in Table 1 (examples according to selected aspects of the invention, comparative steels and steels in the related art (Type 429Nb, SUH409L)) were prepared, and then these steel ingots were heated to 1100°C, and then formed

into hot rolled sheets 4 mm in thickness by hot rolling. Next, the hot rolled sheets were sequentially subjected to hot-rolled-sheet annealing (annealing temperature: 1090°C), pickling, cold rolling (reduction rate: 62.5%), finish annealing (annealing temperature was changed from 900°C to 1220°C as shown in Table 1, and the sheets were held for three minutes at respective temperatures, and then air-cooled, so that the amount of precipitated W was adjusted), and pickling, consequently 1.5 mm thick steel sheets were formed.

[0039] Thermal expansion coefficients of the cold rolled and annealed sheets obtained in this way were examined. Results of examinations are listed together in Table 1.

[0040] Average thermal expansion coefficients between 20°C and 800°C were measured and evaluated as follows.

[0041] The average thermal expansion coefficient between 20°C and 800°C were measured in Ar at the heating rate of 5 °C/min using specimens 1.5 mm thick by 5 mm width by 20 mm long (end faces are polished by emery No.320) and using vertical thermal dilatometer DL-7000 manufactured by SINKU-RIKO, Inc.

[0042] Evaluation criteria are as follows.

[0043] The ferritic stainless in the related art (No.F, G in Table 1 (continuance 1)) has a thermal expansion coefficient of about $12.6 \times 10^{-6} / ^\circ\text{C}$ (average thermal expansion coefficient between 20 and 800°C). Even if heat resistance temperature is improved 30°C (830°C), if about the same thermal strain is exhibited, improvement in heat resistance is expected by 30°C. Thus, effects of it were confirmed by actual thermal fatigue tests. That is, a thermal expansion coefficient α that satisfies $(12.6 \times 10^{-6} / ^\circ\text{C}) \times (800 - 20)^\circ\text{C} > \alpha (830 - 20)^\circ\text{C}$, or a thermal expansion coefficient $\alpha \leq 12.1 \times 10^{-6} / ^\circ\text{C}$ is one of the standards. Naturally, the fact remains that the thermal expansion coefficient α of smaller than $12.6 \times 10^{-6} / ^\circ\text{C}$ is effective for improvement in heat resistance. Thus, the followings were defined: when the steel sheets were measured between 20 and 800°C;

Less than 11.7×10^{-6} : rank A, shown by O in Fig. 1;

11.7×10^{-6} or more and less than 12.1×10^{-6} : rank B, shown by □ in Fig. 1;

12.1x10⁻⁶ or more and less than 12.6x10⁻⁶: lank C, shown by Δ in Fig. 1; and

More than 12.6x10⁻⁶: lank D, shown by ×, * and ♦ in Fig. 1.

[0044] The amount of precipitated W was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). That is, a sample was electrolyzed at constant-current (current density ≤ 20 mA/cm²) using a 10% acetylacetone-base electrolyte (commonly called AA solution). Electrolysis residue in the electrolytic solution was collected by filtration, then fused in alkali (sodium peroxide and metaboric lithium), and then dissolved in an acid and then diluted into a certain quantity by water. The solution was subjected to measurement of the amount of W (W_p) in the solution using the ICP emission spectrometer (Inductively Coupled Plasma Spectrometer). The amount of precipitated W (mass percent) was obtained by the following formula;

$$\text{the amount of precipitated W (mass percent)} = (W_p / \text{sample weight}) \times 100.$$

[0045] Test pieces for evaluation of the amount of precipitated W were sampled from two points adjacent to thermal expansion test pieces in a steel sheet, and an average value of the two was determined as a value of precipitated W.

[0046] Results of measurement are shown in Table 1 and Fig. 1. In Fig. 1, No.A to E, and No.I, J, K, L and M; steel of the invention No.1 to 7 and 20 to 21; and examples in the related art No.P, Q, R, S, T and U are shown. Steel of No.1, 2 and No.B; steel of No.3, 4, 5, C, D, N and O; steel of No.6, 7 and No.E; steel of No.20, 21, I, J; and steel of No.K, L and M are in the same composition, respectively. It is known from Fig. 1 that when W of at least 0.1 exists in the form of the precipitated W, the thermal expansion coefficient is significantly decreased. The comparative steel No.H exhibits a high thermal expansion coefficient even if the amount of W and precipitated W are adjusted within the range of the invention, because it contains Cr of which the amount is out of the range of the invention. The steel No.F and G, which are steel in the related art shown for reference, exhibit high thermal expansion coefficients because the amount of W and precipitated W are out of the range of the invention. In the steel No.K, L and M, since the amount of W exceeds 6%, cracks occurred in bending portions in an adherence bending test (based on JIS B 7778), and consequently workability was bad. In the steel No.N,

since the finish annealing temperature exceeded the upper limit of the range of the invention, orange peel occurred in bending portions in an adherence bending test (based on JIS B 7778), in addition, cracks occurred in some parts. In the steel No.P, Q, R, S, T and U, which are examples in the related art previously developed by the inventors, since the finish annealing temperature is below the lower limit of the range of the invention of the application, the amount of precipitated W is out of the range of the invention, and consequently a high thermal expansion coefficient is exhibited. Any of other steel No.8 to 19 of the invention exhibited a low thermal expansion coefficient.

[0047] From round bars in which compositions and heat treatment conditions of the steel No.3 to 5, and No.C, D and O in Table 1 were implemented, two test pieces as shown in Fig. 2 were prepared and subjected to thermal fatigue test respectively. A condition of the thermal fatigue test was determined according to heat cycle as shown in an upper view of Fig. 3. It was determined that the heating rate from 100°C to 900°C was 4.4 °C/sec, the test pieces were held at 900°C for 10 sec, the cooling rate from 900°C to 100°C was 4.4 °C/sec, and one cycle period was 370 sec. The test was carried out in a way that strain due to free thermal expansion was controlled such that a restraint ratio coefficient was 0.35 between 100°C and 900°C. Assuming that maximum tensile load generated at the fifth cycle, at which a load-strain hysteresis loop become stable, was defined as 100%, and a cycle number at a point where the maximum tensile load was decreased to less than 70% of the maximum tensile load was defined as thermal fatigue life. Results of obtained thermal fatigue life for respective two test pieces were averaged, and an averaged value was determined as the thermal fatigue life. Fig. 4 shows a relation between the amount of precipitated W in ferritic Cr-contained steel and thermal fatigue life of the steel. It is known from Fig. 4 that the thermal fatigue life is remarkably improved as high as 1.4 times or more at the amount of precipitated W of 0.1% or less.

Example 2

[0048] Next, a relation between the amount of precipitated W and the hot-rolled-sheet annealing temperature was investigated. A 50 kg steel ingots having a composition of C of 0.005%, Si of 0.07%, Mn of 1.02%, Cr of 15.2%, Mo of 1.92%, W of 3.02%, Nb of 0.51% and

N of 0.004% were prepared, and then these steel ingots were heated to 1100°C, and then formed into hot rolled sheets 4 mm in thickness. Next, the hot rolled sheets were sequentially subjected to hot-rolled-sheet annealing (annealing temperature was changed from 900°C to 1200°C, and the sheets were held for three minutes at respective temperatures, and then air-cooled), pickling, cold rolling (reduction rate: 62.5%), finish annealing (the sheets were held for three minutes at the finish annealing temperature of 1100°C, and then air-cooled), and pickling, consequently 1.5 mm thick steel sheets were formed.

[0049] The amount of precipitated W in the cold rolled and annealed sheets obtained in this way were measured in the same manner as in the Example 1. Test pieces for evaluation of the amount of precipitated W were sampled from two points in respective steel sheets, and each average value of the two was determined as a value of precipitated W.

[0050] Fig. 5 shows influence of the hot-rolled-sheet annealing temperature on the amount of precipitated W. It is known from Fig. 5 that the hot-rolled-sheet annealing temperature is preferably 950 to 1150°C, and more preferably 1020 to 1150°C.

Table 1

No.	C	Si	Mn	Cr	Mo	W	Nb	N	other	Precipitated W	Average thermal expansion coefficient between 20°C and 800 °C	Finish annealing temperature (°C)	remarks
A	0.012	0.45	0.99	15.2	1.85	1.05	0.55	0.014		0.008	D	1100	Comparative steel
1	0.003	0.35	1.05	14.8	1.88	2.05	0.52	0.008		0.009	C	1100	Example of the invention
2	0.003	0.35	1.05	14.8	1.88	2.05	0.52	0.008		0.092	C	1080	Example of the invention
B	0.003	0.35	1.05	14.8	1.88	2.05	0.52	0.008		1.540	D	1000	Comparative steel
3	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		0.009	A	1180	Example of the invention
4	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		0.035	B	1100	Example of the invention
5	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		0.095	C	1080	Example of the invention
C	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		0.580	D	1010	Comparative steel
D	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		1.850	D	950	Comparative steel
6	0.002	0.08	0.99	15.1	1.87	4.98	0.49	0.004		0.018	A	1200	Example of the invention
7	0.002	0.08	0.99	15.1	1.87	4.98	0.49	0.004		0.041	B	1150	Example of the invention
E	0.002	0.08	0.99	15.1	1.87	4.98	0.49	0.004		1.980	D	1010	Comparative steel

Table 1 (continuance 1)

No.	C	Si	Mn	Cr	Mo	W	Nb	N	other	Precipitated W	Average thermal expansion coefficient between 20°C and 800 °C	Finish annealing temperature (°C)	remarks
8	0.002	0.56	0.55	30.5	Not added	3.05	Not added	0.002		0.018	A	1090	Example of the invention
9	0.015	1.84	1.05	9.5	1.5	2.35	0.65	0.015		0.011	C	1090	Example of the invention
10	0.004	0.15	1.51	24.5	Not added	2.68	Not added	0.005	Ti/0.25	0.032	B	1090	Example of the invention
11	0.005	0.04	1.05	20.8	Not added	4.58	0.35	0.005	Zr/0.12	0.012	A	1090	Example of the invention
12	0.002	0.07	0.09	22.5	0.54	3.05	0.25	0.005	Al/0.15	0.021	A	1150	Example of the invention
13	0.005	0.25	1.08	15.4	1.85	2.99	0.48	0.005	V/0.15, Al/0.05	0.009	A	1050	Example of the invention
14	0.004	0.25	0.25	9.5	3.05	3.07	0.45	0.005		0.033	B	1090	Example of the invention
15	0.012	0.04	0.15	16.5	Not added	3.01	0.25	0.015	Ti/0.08, Ni/0.51, Cu/1.25	0.014	B	1070	Example of the invention
16	0.011	0.55	0.35	16.9	Not added	3.08	0.35	0.009	Cu/0.43, Co/0.12	0.007	B	1080	Example of the invention
17	0.004	0.85	0.98	14.9	1.87	2.85	0.45	0.008	B/0.0005, Ca/0.0015	0.007	A	1150	Example of the invention
18	0.005	0.84	0.88	16.4	1.68	3.07	0.65	0.007	Mg/0.0008	0.015	A	1150	Example of the invention
19	0.007	0.88	0.85	16.4	1.68	3.09	0.5	0.007	REM/0.08	0.025	A	1150	Example of the invention
F	0.007	0.63	0.41	11.2	Not added	<0.02	0.004	0.007	Ti/0.21	<0.005	D	900	SUH409L
G	0.014	1.04	0.45	14.1	Not added	<0.02	0.45	0.007		<0.005	D	1000	Type 429Nb
H	0.004	0.35	1.09	5.4	Not added	2.25	0.45	0.004		0.009	D	1150	Comparative steel

Table 1 (continuance 2)

No.	C	Si	Mn	Cr	Mo	W	Nb	N	others	Precipitated W	Average thermal expansion coefficient between 20°C and 800 °C	Finish annealing temperature (°C)	remarks
20	0.004	0.08	0.89	14.9	1.89	5.85	0.48	0.005		0.021	A	1190	Example of the invention
21	0.004	0.08	0.89	14.9	1.89	5.85	0.48	0.005		0.086	C	1080	Example of the invention
I	0.004	0.08	0.89	14.9	1.89	5.85	0.48	0.005		0.950	D	1000	Comparative example
J	0.004	0.08	0.89	14.9	1.89	5.85	0.48	0.005		2.220	D	980	Comparative example
K	0.004	0.06	1.03	15.1	1.92	6.18	0.50	0.005		0.028	A	1180	Comparative example*1
L	0.004	0.06	1.03	15.1	1.92	6.18	0.50	0.005		0.091	C	1040	Comparative example*1
M	0.004	0.06	1.03	15.1	1.92	6.18	0.50	0.005		2.240	D	980	Comparative example*1
N	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		0.009	A	1220	Comparative example*2
O	0.005	0.07	1.02	15.2	1.92	3.02	0.51	0.004		0.110	D	1040	Comparative example*3
P	0.004	0.21	0.41	12.6	1.51	2.51	0.31	0.003	Ni/0.03	1.660	D	1000	Example in the related art*4
Q	0.008	0.15	0.05	13.1	1.61	2.11	0.85	0.004	Ni/0.03, Zr/0.28	1.490	D	1000	Example in the related art*4
R	0.004	0.33	1.78	12.7	1.61	2.59	0.49	0.005	Ni/0.55	1.700	D	1000	Example in the related art*4
S	0.003	0.05	0.35	16.5	1.93	2.81	0.45	0.003	Al/0.58	1.790	D	1000	Example in the related art*5
T	0.005	0.68	1.2	18.2	2.22	3.12	0.50	0.006	Zr/0.12	1.140	D	1000	Example in the related art*5
U	0.009	0.08	0.57	18.8	1.21	3.52	0.45	0.009	Mg/0.012	1.280	D	1000	Example in the related art*5

*1: cracks occurred in the adherence bending test (based on JIS B 7778)

*2: surface roughness (orange peel) occurred in a bending portion, and in some parts, cracks occurred in the adherence bending test (based on JIS B 7778)

*3: for thermal fatigue test

*4: JP-A-2002-212685 (Table 1, steel numbers 22, 23 and 25)

*5: JP-A-2004-76154, Japanese Patent Application No.2003-172437 (Table 1, numbers 3, 7 and 12)

Fig. 1

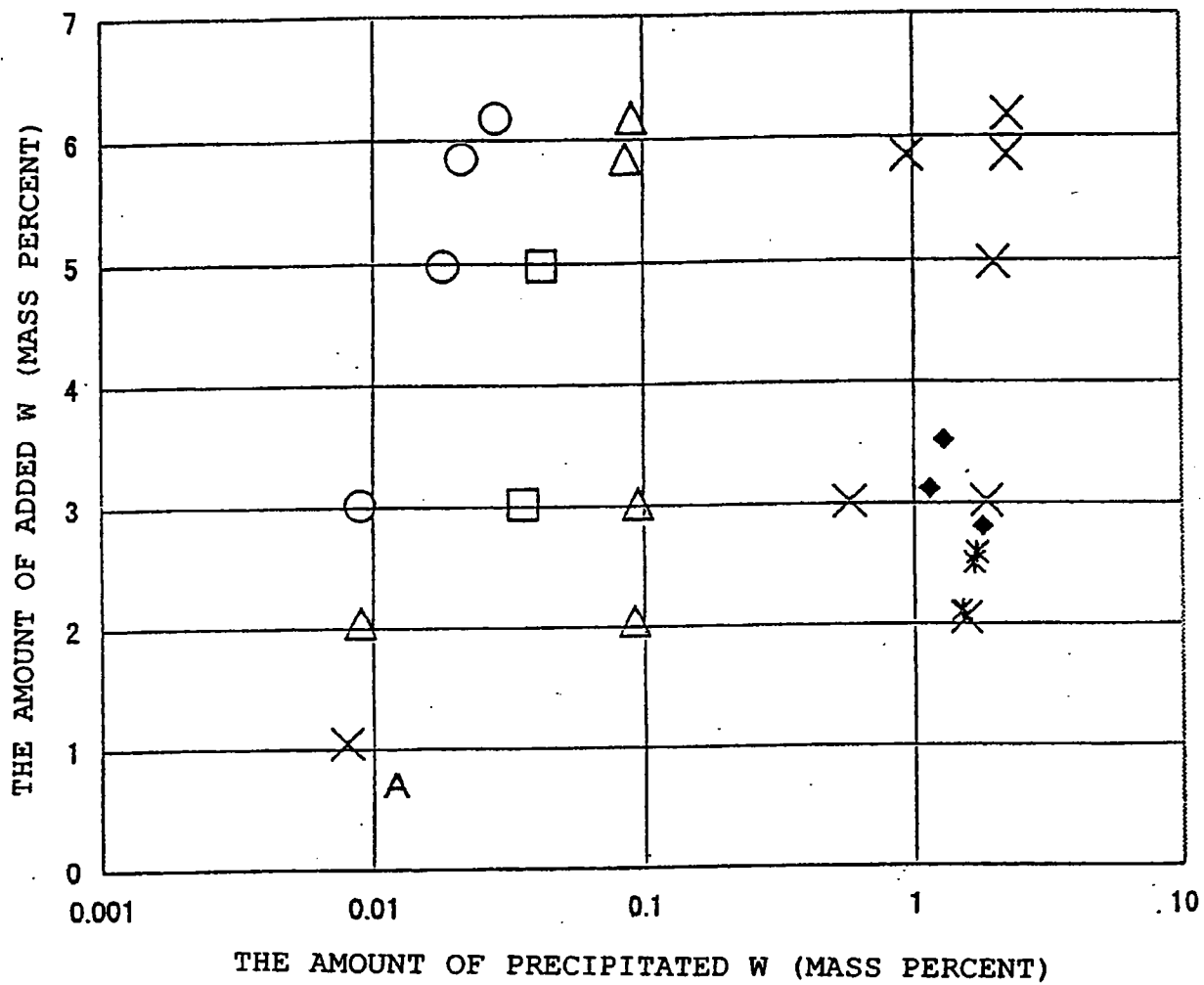


Fig. 2

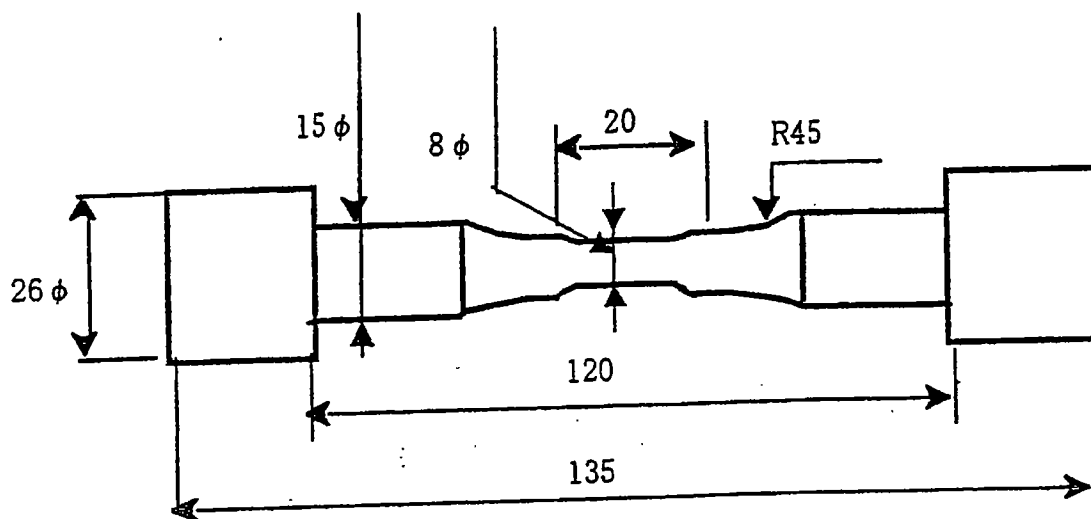


Fig. 3

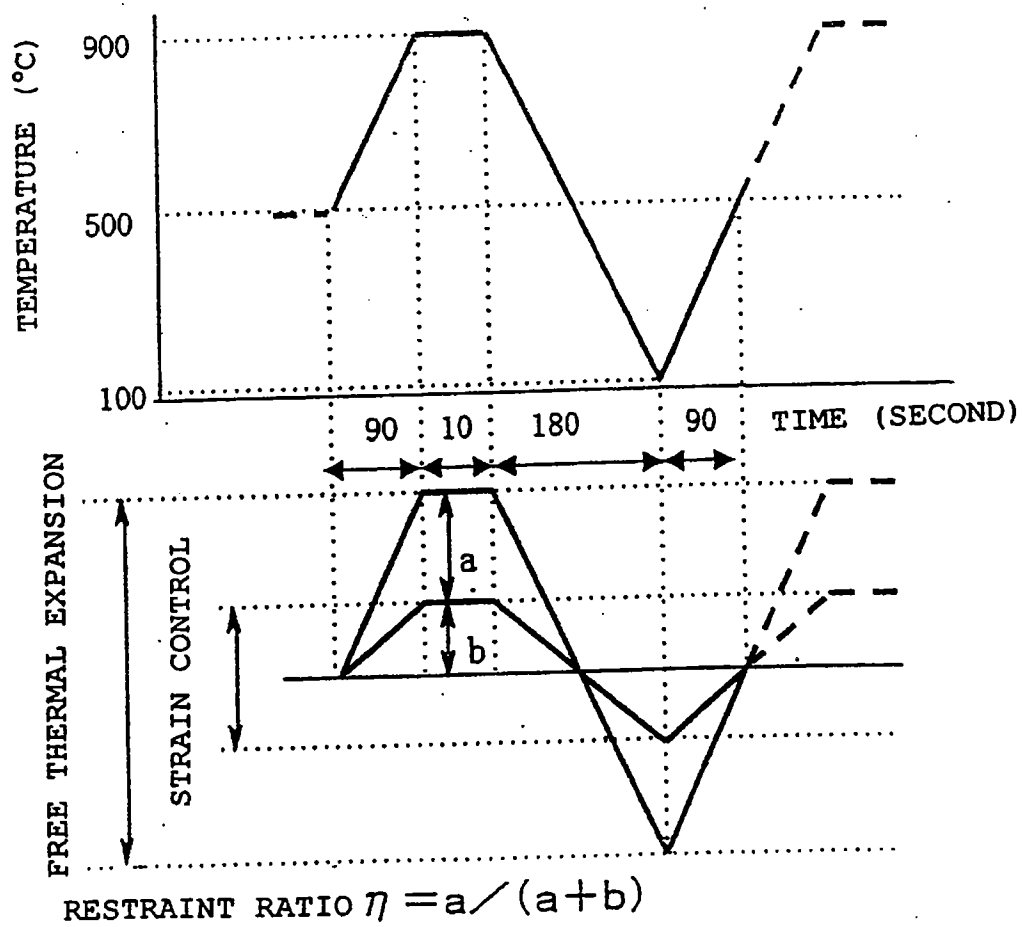


Fig. 4

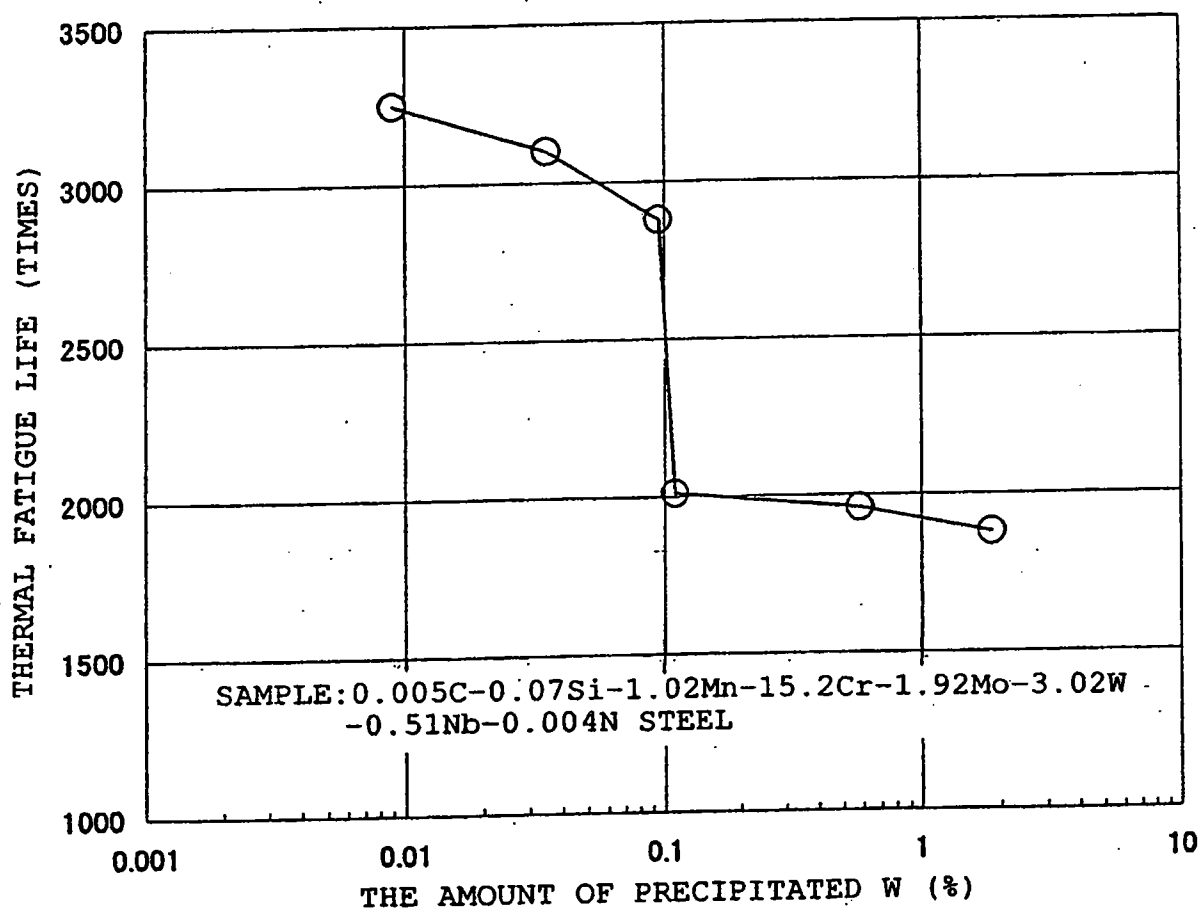
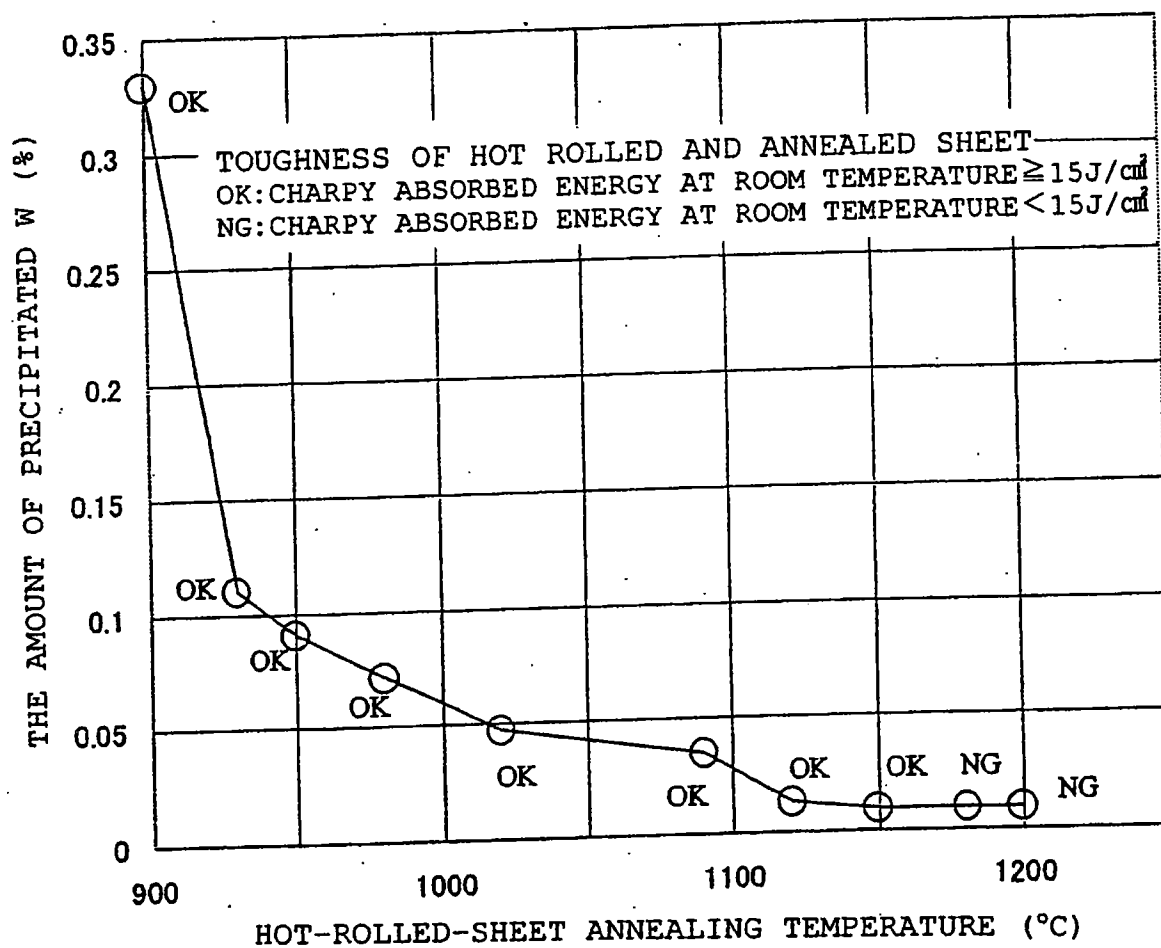


Fig. 5



United States Patent [19]

Kawabata et al.

[11] Patent Number: 5,626,694

[45] Date of Patent: May 6, 1997

[54] **PROCESS FOR THE PRODUCTION OF STAINLESS STEEL SHEETS HAVING AN EXCELLENT CORROSION RESISTANCE**

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[73] Assignee: Kawasaki Steel Corporation, Japan

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§ 371 Date: Sep. 22, 1995

§ 102(e) Date: Sep. 22, 1995

[87] PCT Pub. No.: WO95/20683

PCT Pub. Date: Mar. 8, 1995

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[52] U.S. Cl. 148/609; 148/610; 148/654

[58] Field of Search 148/609, 610,
148/654, 661

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Primary Examiner—Deborah Yee

Attorney, Agent, or Firm—Austin R. Miller

[57] **ABSTRACT**

This invention relates to a process for the production of stainless steel sheets and proposes a process for the production of stainless steel sheets having a more excellent corrosion resistance as compared with the conventional one without trimming the steel sheet surface after annealing-pickling by preventing the chapping of steel sheet surface created in the production of present stainless steel sheet, particularly stainless steel sheets having extreme-low amounts of C, S, O.

For this purpose, according to the invention, a starting material of stainless steel containing C: not more than 0.01 wt %, S: not more than 0.005 wt % and O: not more than 0.005 wt % is subjected to a hot rolling at a draft below 830° C. of not less than 30%, cooled at a cooling rate of not less than 25° C. sec, coiled below 650° C. and then annealed and pickled.

7 Claims, 3 Drawing Sheets

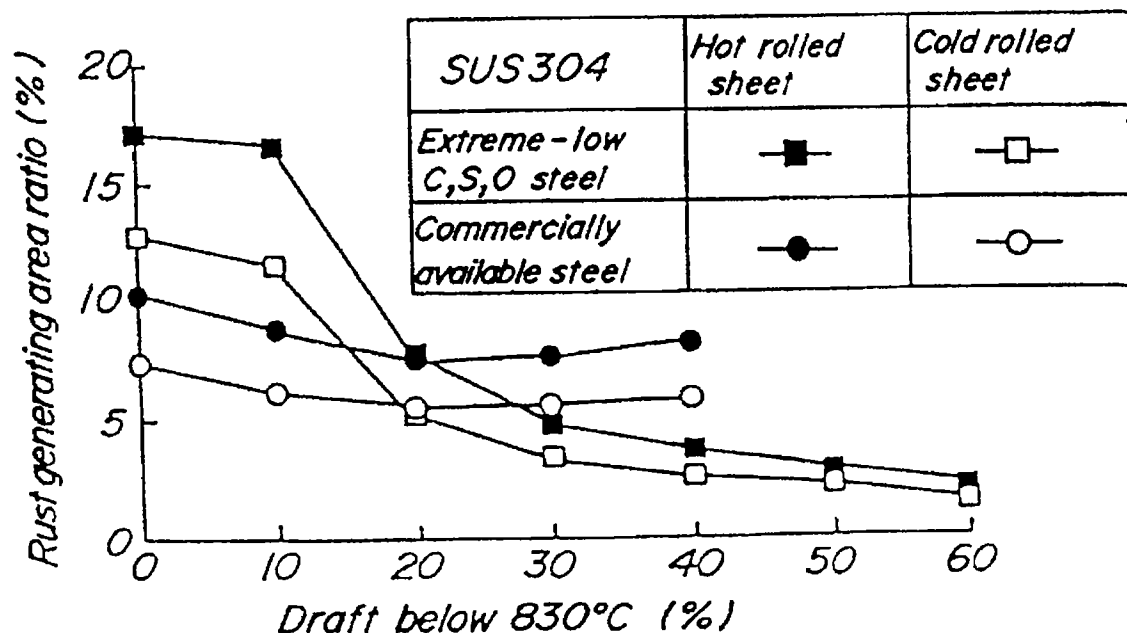


FIG. 1

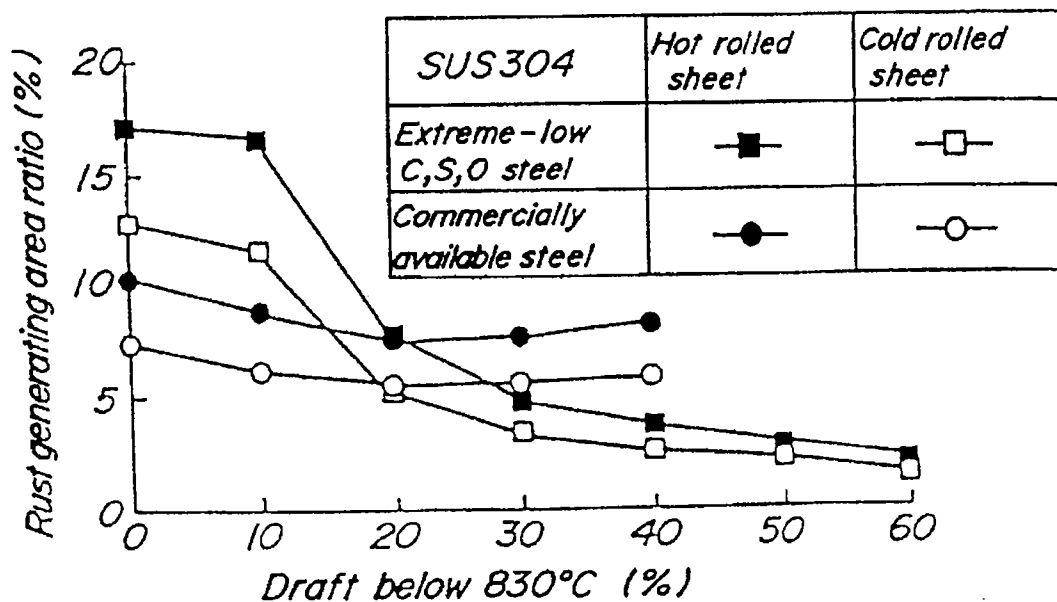


FIG. 2

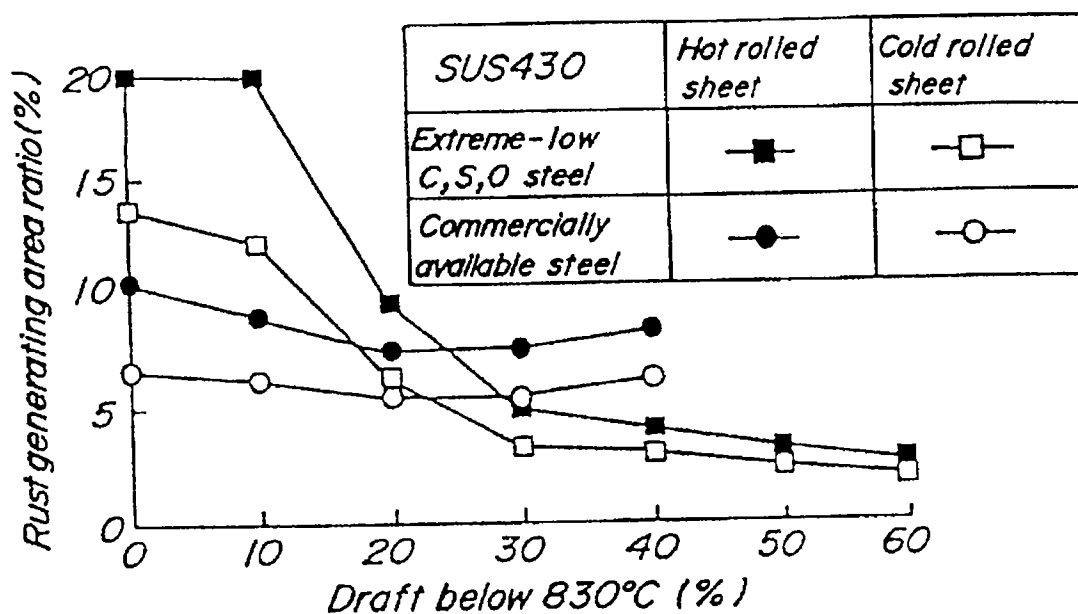


FIG. 3

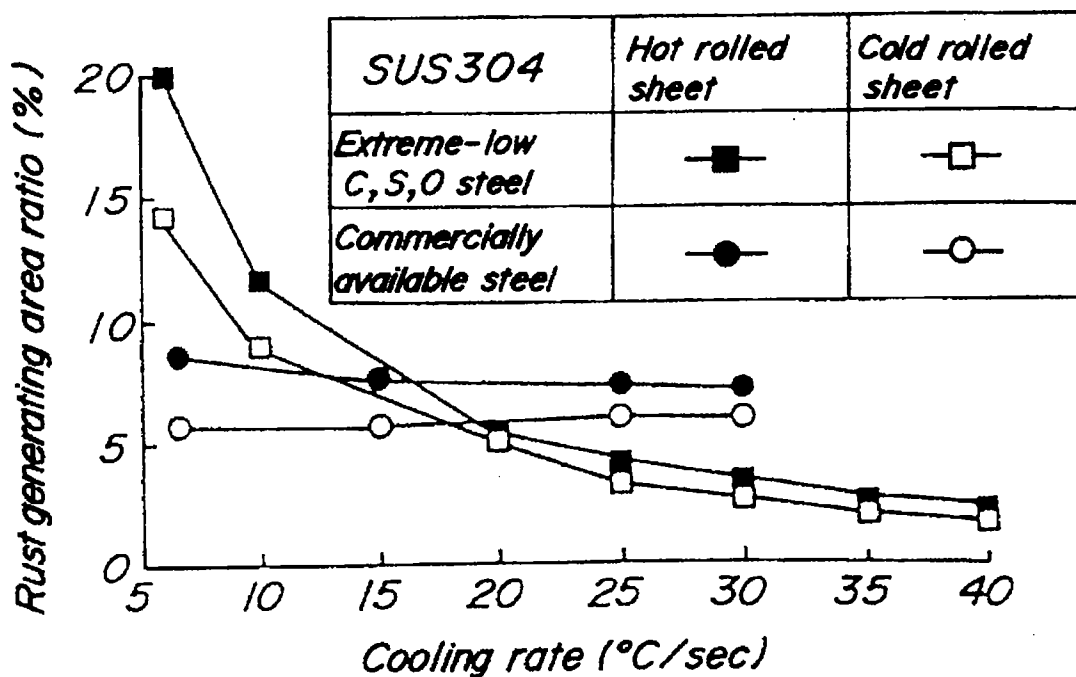


FIG. 4

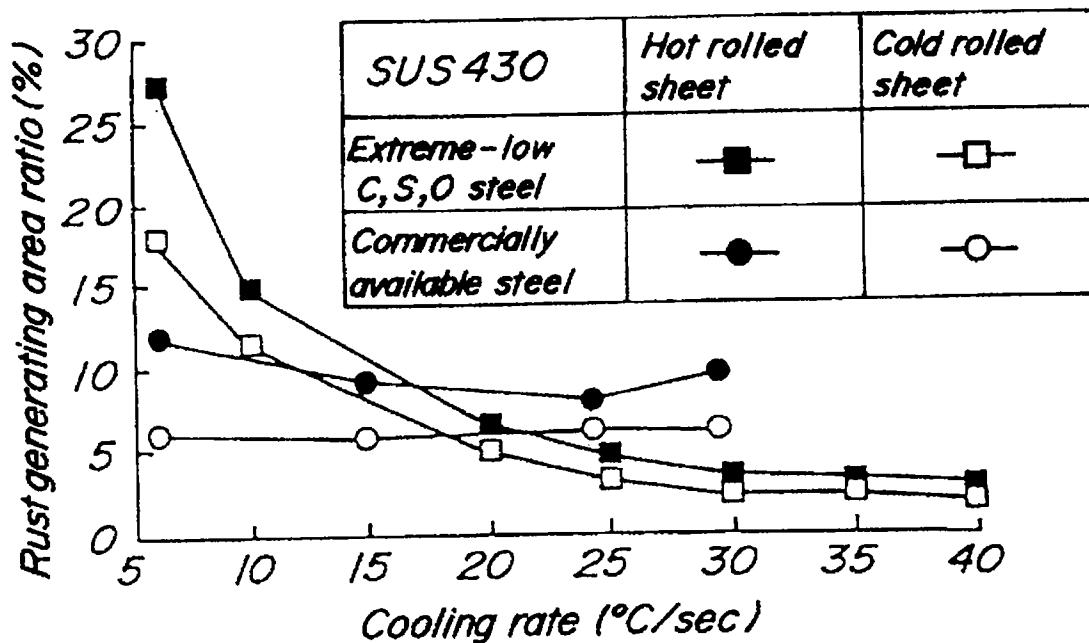
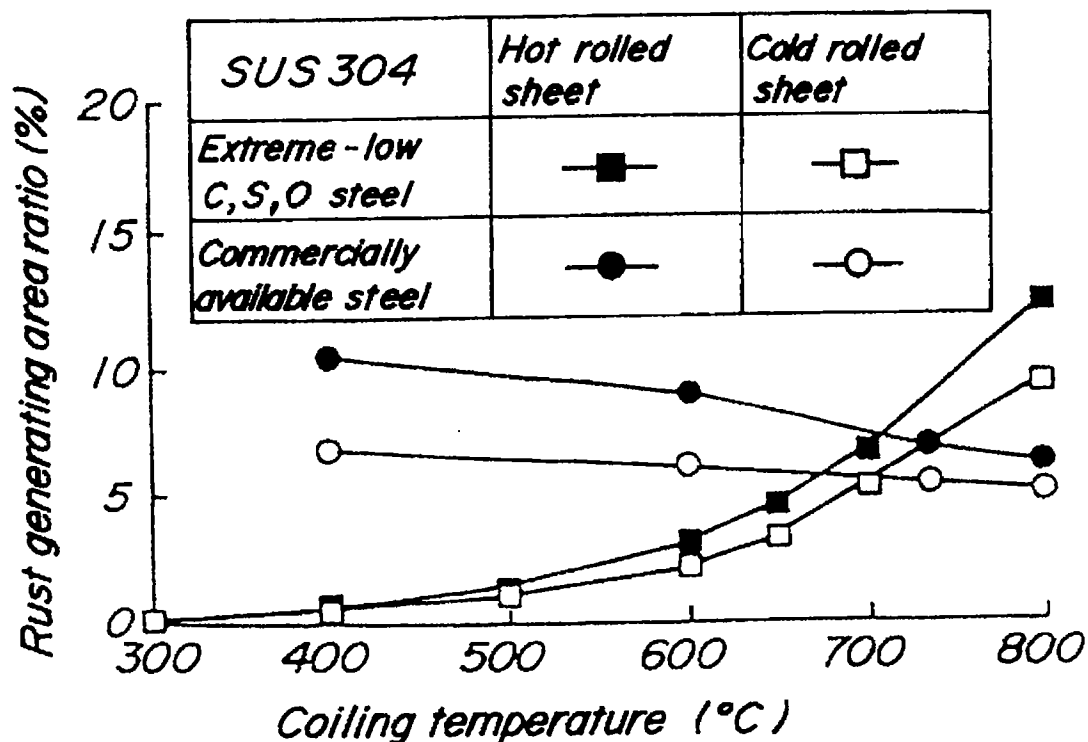
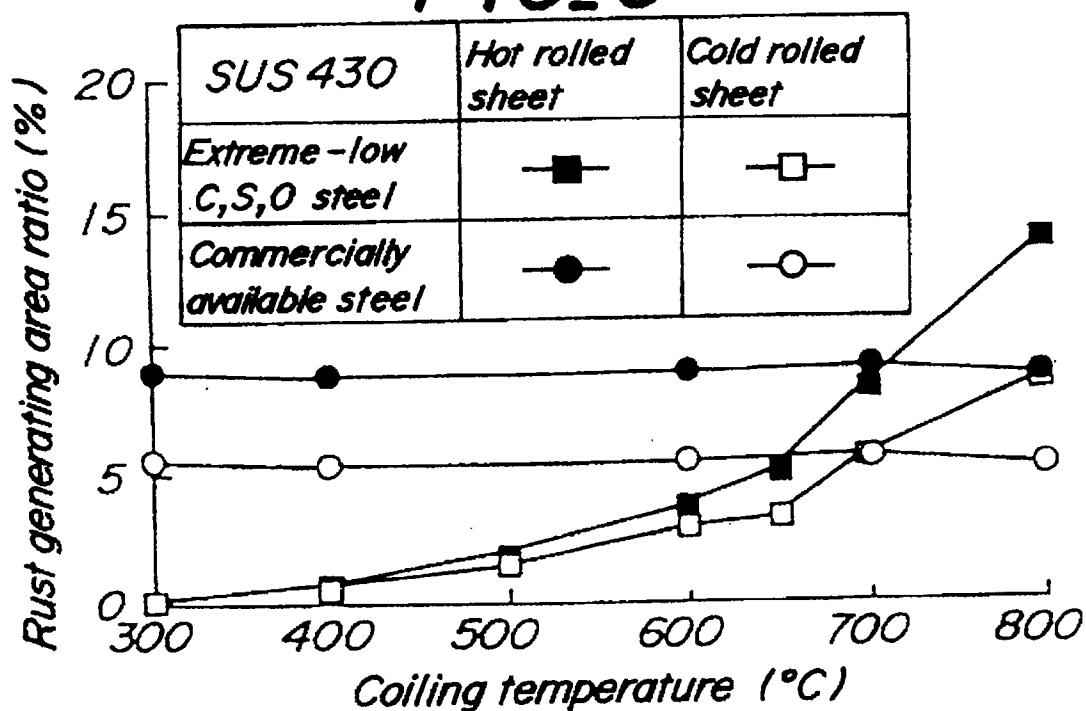


FIG. 5**FIG. 6**

PROCESS FOR THE PRODUCTION OF STAINLESS STEEL SHEETS HAVING AN EXCELLENT CORROSION RESISTANCE

TECHNICAL FIELD

This invention relates to a process for the production of stainless steel, and more particularly to a process for the production of stainless steel sheets having an excellent corrosion resistance.

BACKGROUND ART

Stainless steel sheets are excellent in the corrosion resistance under various corrosive environments and are widely used as building materials, materials for automobiles, materials for chemical plants and so on. Recently, there are observed many examples of service environments which are becoming more severe and the stainless steel sheet is demanded to have a more excellent corrosion resistance. On the other hand, stainless steels which take too much labor in their production, even though the corrosion resistance is excellent, are unfavorable to stainless steel manufacturers, so that it is desired that the stainless steel is excellent in the productivity, particularly hot workability.

Under the above circumstances, it has recently become possible to reduce impurities in steel with the advance of steel-making techniques, so as to improve the above corrosion resistance and hot workability by decreasing C, S and O in the stainless steel. For example, JP-B-60-57501 discloses a method of improving anti-corrosion in sea water and hot workability by decreasing C, S and O, and JP-B-2-46662 and JP-B-2-14419 disclose a method of likely improving the hot workability.

According to the above conventional improving techniques, however, there may be created remarkable chapping in a surface of stainless steel sheet after hot rolling-annealing-pickling. Such a chapping falls down during cold rolling to remain as a scab-like defect after the cold rolling, which undesirably deteriorates the corrosion resistance in hot rolled steel sheet and cold rolled steel sheet.

Of course, it has been attempted to trim the chapped surface of the steel sheet by means of a grinder or the like, which brings about the decrease of productivity and the rise of cost and is not an advantageous countermeasure. For this end, it is strongly desired to establish a technique of not creating the above chapping on the surface of the stainless steel sheet after annealing-pickling.

DISCLOSURE OF INVENTION

It is, therefore, a main object of the invention to solve the aforementioned problems in the production of the present stainless steel sheets, particularly stainless steel sheets having extreme-low amounts of C, S and O and to provide a process for the production of stainless steel sheets having more improved corrosion resistance as compared with the conventional ones without trimming the surface of the steel sheet after annealing-pickling.

In order to achieve the above object, there have been made various studies with respect to causes of creating the chapping on the surface of the conventional stainless steel sheet after annealing-pickling and also means for the prevention thereof has been examined. As a result, the following facts have been confirmed. That is,

1) The chapping of the steel sheet surface is caused due to the fact that Cr-removed layer formed in the annealing is eroded with an acid to form unevenness on the surface of the steel sheet.

2) The Cr-removed layer grows as an amount of scale (Fe_3O_4) in the hot rolled sheet becomes large.

3) The Cr-removed layer grows as an adhesion property of scale (Fe_3O_4) in the hot rolled sheet to iron matrix becomes strong.

4) The scale Fe_3O_4 in the hot rolled sheet is formed at a relatively low temperature below 830°C .

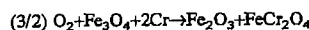
From the above facts, the inventors have noticed the following:

5) In order to prevent the chapping of the steel sheet surface, it is effective to decrease the amount of scale Fe_3O_4 and to lower the adhesion property to iron matrix.

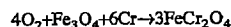
6) In order to decrease the amount of scale Fe_3O_4 and lower the adhesion property to iron matrix, it is effective to control a finish temperature of hot rolling, and a cooling rate and a coiling temperature followed thereto.

Although a mechanism of forming the Cr-removed layer through the aforementioned scale (Fe_3O_4) is not necessarily clear, the followings are considered.

In general, the annealing of a cold rolled stainless steel sheet is carried out in a relatively high temperature and low oxygen atmosphere. If the stainless steel is annealed in such an atmosphere, it is oxidized to form Cr_2O_3 , but since this Cr_2O_3 has a protection property to oxidation, the oxidation rate gradually lowers and finally the Cr-removed layer hardly forms on the surface of the steel sheet. In the hot rolling of the stainless steel (hereinafter abbreviated as hot rolling in some cases), the atmosphere is different from that in the above annealing, so that scale composed mainly of Fe_3O_4 is formed. When this Fe_3O_4 scale has a strong adhesion property to iron matrix, the scale absorbs Cr from the iron matrix in the annealing according to the following reaction:



or



Thus, when Fe_3O_4 is existent on the surface, Cr is consumed without the formation of Cr_2O_3 having a protection property to oxidation and hence it is considered to considerably promote the growth of the Cr-removed layer.

Further, the reason why the Fe_3O_4 scale in the hot rolled sheet grows at a relatively low temperature below 830°C is considered due to the fact that when the steel sheet is cooled in air after the hot rolling, Fe is sufficiently rapidly oxidized, while Cr in steel is slow in the diffusion and can not diffuse up to the surface and hence the main component of the scale is Fe. And also, the reason why the degree of surface chapping after the pickling in stainless steel containing extreme-low levels of C, S and O is larger than that of stainless steel containing approximately usual level of C, S and O is considered due to the fact that the adhesion property of scale to iron matrix is high in the stainless steel containing extreme-low levels of C, S and O.

The invention is based on the above knowledge. That is, the essential point and construction of the invention are as follows.

(1) A process for the production of stainless steel sheets having an excellent corrosion resistance, characterized in that a starting material of stainless steel containing C: not more than 0.01 wt %, S: not more than 0.005 wt % and O: not more than 0.005 wt % is subjected to a hot rolling at a draft below 830°C , of not less than 30%, and the resulting hot rolled sheet is coiled at a cooling rate of not less than 25°

C./sec and coiled at a temperature of not higher than 650° C. and thereafter is subjected to annealing and pickling (first embodiment).

(2) A process for the production of stainless steel sheets having an excellent corrosion resistance, characterized in that a starting material of stainless steel containing C: not more than 0.01 wt %, S: not more than 0.005 wt % and O: not more than 0.005 wt % is subjected to a hot rolling at a draft below 830° C. of not less than 30% to a thickness of not more than 1.5 mm, and the resulting hot rolled sheet is coiled at a cooling rate of not less than 25° C./sec and coiled at a temperature of not higher than 650° C. and thereafter is successively subjected to annealing, pickling and skin pass rolling at a draft of not more than 20% (second embodiment).

(3) A process for the production of stainless steel sheets having an excellent corrosion resistance, characterized in that a starting material of stainless steel containing C: not more than 0.01 wt %, S: not more than 0.005 wt % and O: not more than 0.005 wt % is subjected to a hot rolling at a draft below 830° C. of not less than 30%, and the resulting hot rolled sheet is coiled at a cooling rate of not less than 25° C./sec and coiled at a temperature of not higher than 650° C. and thereafter is subjected to annealing and pickling, and then subjected to a cold rolling at a total draft of more than 20% in a cold rolling installation provided with work rolls having a roll diameter of not less than 250 mm (third embodiment).

(4) A process according to anyone of the first to third embodiments, wherein a ferritic stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 5 wt %, Cr: 9–50 wt %, Ni: less than 5 wt %, and the remainder being Fe and inevitable impurities is used as the starting material (fourth embodiment).

(5) A process according to anyone of the first to third embodiments, wherein a ferritic stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 5 wt %, Cr: 9–50 wt %, Ni: less than 5 wt %, and further containing one or more elements selected from the group consisting of Ti: 0.01–1.0 wt %, Nb: 0.01–1.0 wt %, V: 0.01–1.0 wt %, Zr: 0.01–1.0 wt %, Ta: 0.01–1.0 wt %, Co: 0.1–5 wt %, Cu: 0.1–5 wt %, Mo: 0.1–5 wt %, W: 0.1–5 wt %, Al: 0.005–5.0 wt %, Ca: 0.0003–0.01 wt % and B: 0.0003–not more than 0.01 wt %, and the remainder being Fe and inevitable impurities is used as the starting material (fifth embodiment).

(6) A process according to anyone of the first to third embodiments, wherein an austenitic stainless steel or dual-phase stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 20 wt %, Cr: 9–50 wt %, Ni: 5–20 wt %, N: not more than 0.2 wt %, and the remainder being Fe and inevitable impurities is used as the starting material (sixth embodiment).

(7) A process according to anyone of the first to third embodiments, wherein an austenitic stainless steel or dual-phase stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 20 wt %, Cr: 9–50 wt %, Ni: 5–20 wt %, N: not more than 0.2 wt %, and further containing one or more elements selected from the group consisting of Ti: 0.01–1.0 wt %, Nb: 0.01–1.0 wt %, V: 0.01–1.0 wt %, Zr: 0.01–1.0 wt %, Ta: 0.01–1.0 wt %, Co: 0.1–5 wt %, Cu: 0.1–5 wt %, Mo: 0.1–5 wt %, W: 0.1–5 wt %, Al: 0.005–5.0 wt %, Ca: 0.0003–0.01 wt % and B:

0.0003–not more than 0.01 wt %, and the remainder being Fe and inevitable impurities is used as the starting material (seventh embodiment).

As the selective addition element in the fifth or seventh embodiment, it is effective to use elements in each group of ① Ti, Nb, V, Zr, Ta, ② Co, Cu, ③ Mo, W, ④ Al, ⑤ Ca and ⑥ B alone or add a combination of two or more elements selected from each group of ①–⑥.

The reason why the invention is limited to the above essential point and construction will be described below.

Draft below 830° C. of not less than 30%;

In the extreme-low C, S, O stainless steel, the working in the above range acts to lower the adhesion property between scale and iron matrix by generating cracks in Fe₃O₄ scale produced in the hot rolling, whereby the growth of the Cr-removed layer can be controlled in the annealing to enhance the corrosion resistance.

Thus, the draft below 830° C. particularly promoting the growth of the Fe₃O₄ scale is important. When the value of the draft is less than 30%, sufficient strain amount is not given and hence sufficient cracks for the improvement of corrosion resistance can not be introduced. Therefore, the draft below 830° C. is necessary to be not less than 30%.

Moreover, the term "draft" used herein is a ratio of sheet thickness after hot rolling to thickness of the steel sheet at 830° C. and may be attained by plural times of rolling or single rolling. And also, it is desirable that the rolling temperature is low, but when the rolling temperature is too low, surface defects in the hot rolling increases and hence the unevenness after the pickling is increased by factors other than the Cr-removed layer produced through oxidation in the annealing. Therefore, it is desirable that the rolling is carried out at a temperature of not lower than 700° C.

The influence of the draft below 830° C. upon corrosion resistance of each of hot rolled sheet and cold rolled sheet is shown in FIG. 1 using extreme-low C, extreme-low S, extreme-low O steel (hereinafter referred to as extreme-low CSO steel simply, C: 0.0050 wt %, S: 0.0040 wt %, O: 0.0040 wt %) and commercially available steel (C: 0.0500 wt %, S: 0.0082 wt %, O: 0.0068 wt %) as two kinds of SUS 304, and in FIG. 2 using extreme-low CSO steel (C: 0.0020 wt %, S: 0.0038 wt %, O: 0.0030 wt %) and commercially available steel (C: 0.0520 wt %, S: 0.0068 wt %, O: 0.0065 wt %) as two kinds of SUS 430, respectively. Moreover, the hot rolled sheet is obtained by subjecting to hot rolling (cooling rate: 40° C./sec, coiling temperature: 600° C.)-annealing-pickling, and the cold rolled sheet is obtained by subjecting to hot rolling (cooling rate: 45° C./sec, coiling temperature: 600° C.)-annealing-pickling-cold rolling (draft at roll diameter of 250 mm: 50%)-annealing-pickling. The corrosion resistance is evaluated by rust generating area ratio after 2 days of CCT test.

In these figures, symbol ■ is a hot rolled sheet of the extreme-low CSO steel, symbol □ is a cold rolled sheet of the extreme-low CSO steel, symbol ● is a hot rolled sheet of the commercially available steel, and symbol ○ is a cold rolled sheet of the commercially available steel. From these figures, it is understood that when the draft below 830° C. is not less than 30%, there is particularly an effect of considerably improving the corrosion resistance for the extreme-low CSO steel.

Cooling rate of not less than 25° C./sec;

When the cooling rate is increased after the completion of the hot rolling, not only the amount of scale produced after the hot rolling is decreased, but also the adhesion property between scale and iron matrix is decreased based on the difference of thermal expansion to the iron matrix, so that

the increase of the cooling rate is effective for the peeling of the scale. Thus, the growth of the Cr-removed layer can be controlled in the subsequent annealing to enhance the corrosion resistance.

Since such an effect is not obtained at a cooling rate of less than 25° C./sec. the cooling rate is limited to not less than 25° C./sec. Moreover, the preferable cooling rate is not less than 40° C./sec.

The influence of the cooling rate after the completion of the hot rolling upon corrosion resistance of each of hot rolled sheet and cold rolled sheet is shown in FIG. 3 using extreme-low CSO steel (C: 0.0050 wt %, S: 0.0040 wt %, O: 0.0040 wt %) and commercially available steel (C: 0.0500 wt %, S: 0.0082 wt %, O: 0.0068 wt %) as two kinds of SUS 304, and in FIG. 4 using extreme-low CSO steel (C: 0.0020 wt %, S: 0.0038 wt %, O: 0.0030 wt %) and commercially available steel (C: 0.0520 wt %, S: 0.0068 wt %, O: 0.0065 wt %) as two kinds of SUS 430, respectively. Moreover, the hot rolled sheet is obtained by subjecting to hot rolling (draft below 830° C.:30%, coiling temperature: 550° C.)-annealing-pickling, and the cold rolled sheet is obtained by subjecting to hot rolling (draft below 830° C.:35%, coiling temperature: 550° C.)-annealing-pickling-cold rolling (draft at roll diameter of 300 mm: 50%)-annealing-pickling. The corrosion resistance is evaluated by rust generating area ratio after 2 days of CCT test.

In these figures, symbol ■ is a hot rolled sheet of the extreme-low CSO steel, symbol □ is a cold rolled sheet of the extreme-low CSO steel, symbol ● is a hot rolled sheet of the commercially available steel, and symbol ○ is a cold rolled sheet of the commercially available steel. From these figures, it is understood that when the cooling rate after the hot rolling is not less than 25° C./sec. there is particularly an effect of considerably improving the corrosion resistance for the extreme-low CSO steel.

Coiling temperature of not higher than 650° C.;

The coiling temperature affects the adhesion property between scale and iron matrix and the amount of scale produced after the coiling. When the coiling temperature exceeds 650° C., it is insufficient to weaken the adhesion property between scale and iron matrix and also the amount of scale produced after the coiling is increased. For this end, the growth of the Cr-removed layer is promoted at the subsequent annealing to degrade the corrosion resistance. Therefore, in order to control the Cr-removed layer to improve the corrosion resistance, it is necessary to restrict the coiling temperature to not higher than 650° C. Although the coiling temperature is desired to be low, if it is too low, the surface defect in the coiling is increased to increase the unevenness after the pickling based on factors other than the Cr-removed layer, so that the coiling is desirable to be carried out at a temperature of not lower than 200° C.

The influence of the coiling temperature after the hot rolling upon corrosion resistance of each of hot rolled sheet and cold rolled sheet is shown in FIG. 5 using extreme-low CSO steel (C: 0.0050 wt %, S: 0.0040 wt %, O: 0.0040 wt %) and commercially available steel (C: 0.0500 wt %, S: 0.0082 wt %, O: 0.0068 wt %) as two kinds of SUS 304, and in FIG. 6 using extreme-low CSO steel (C: 0.0020 wt %, S: 0.0038 wt %, O: 0.0030 wt %) and commercially available steel (C: 0.0520 wt %, S: 0.0068 wt %, O: 0.0065 wt %) as two kinds of SUS 430, respectively. Moreover, the hot rolled sheet is obtained by subjecting to hot rolling (draft below 830° C.:40%, cooling rate: 40° C./sec)-annealing-pickling, and the cold rolled sheet is obtained by subjecting to hot rolling (draft below 830° C.: 40%, cooling rate: 45° C./sec)-annealing-pickling-cold rolling (draft at roll diameter of

250 mm: 45%)-annealing-pickling. The corrosion resistance is evaluated by rust generating area ratio after 2 days of CCT test.

In these figures, symbol ■ is a hot rolled sheet of the extreme-low CSO steel, symbol □ is a cold rolled sheet of the extreme-low CSO steel, symbol ● is a hot rolled sheet of the commercially available steel, and symbol ○ is a cold rolled sheet of the commercially available steel. From these figures, it is understood that when the coiling temperature after the hot rolling and quenching is not higher than 650° C., there is particularly an effect of considerably improving the corrosion resistance for the extreme-low CSO steel.

Thickness of hot rolled sheet of not more than 1.5 mm and draft of skin pass rolling of not more than 20%;

In general, stainless steel sheets having a thickness of not more than 1.5 mm are produced by subjecting the hot rolled sheet to a cold rolling. Of course, cold rolled stainless steel sheets can be produced by applying the invention to the above process, but it is recently attempted to produce stainless steel sheets having a thickness of not more than 1.5 mm by so-called hot rolling-annealing-pickling steps with omission of cold rolling step in accordance with the increase of capacity of hot rolling mill and the reduction of slab thickness. If the steel sheet is produced at such steps according to the conventional technique, there is a problem that the surface chapping is still retained after the pickling to lower the corrosion resistance as compared with the conventional cold rolled sheet.

On the other hand, the process according to the invention develops a remarkable effect when the steel sheet is produced at the above steps, particularly when the skin pass rolling is carried out at a draft of not more than 20% for the hot rolled sheet having a thickness of not more than 1.5 mm. That is, the thickness of the hot rolled sheet is restricted to not more than 1.5 mm and the draft of the skin pass rolling is restricted to not more than 20%, preferably 1-15%. According to the invention process, it is possible to produce stainless steel corresponding to the conventional bright-finished cold rolled sheet at the above steps.

Work roll diameter of not less than 250 mm in a cold rolling installation and total draft of more than 20% through work rolls;

In general, stainless steel cold rolled sheets are produced by cold rolling with rolls having a diameter of not more than 100 mm, but the productivity is very low as compared with a tandem rolling mill using a large-size roll usually used in the rolling of general-purpose steel. For this end, there has recently been increased a case of subjecting the stainless steel to cold rolling through the tandem rolling mill. However, when using the tandem rolling mill, there is a problem that surface defect is apt to be caused by falling down the unevenness of the surface before the cold rolling to lower the corrosion resistance.

The invention process develops a remarkable effect at the above step, particularly when cold rolling is carried out at a total draft of more than 20% through work rolls having a diameter of not less than 250 mm, so that the work roll diameter in the cold rolling installation is restricted to not less than 250 mm and the total draft through the work rolls is restricted to more than 20%. After such a cold rolling, annealing-pickling or bright annealing may be conducted according to the usual manner.

According to the invention, production conditions other than those in the above steps are not particularly critical, and may be within usual manner. For example, it is favorable that the heating temperature of slab is 1000°-1300° C., and the annealing temperature is 700°-1300° C., and the pick-

ling condition is an immersion in mixed acid (nitric acid and hydrofluoric acid) after the immersion in sulfuric acid. Further, it is preferable to conduct a passivating treatment after the pickling in order to more improve the corrosion resistance.

The chemical composition of stainless steel preferably applied to the invention will be described below.

C: not more than 0.010 wt %, S: not more than 0.0050 wt %, O: not more than 0.0050 wt %;

These elements lower not only the corrosion resistance of stainless steel but also the hot workability, so that it is desired to reduce amounts of these elements. Particularly, when C, S and O are included in amounts of more than 0.0100 wt %, more than 0.0050 wt % and 0.0050 wt %, respectively, the corrosion resistance is considerably degraded, and good corrosion resistance can not be obtained even if stainless steel is produced under the conditions according to the invention process. Therefore, the amounts of these elements are restricted to C: not more than 0.0100 wt %, S: not more than 0.0050 wt % and O: not more than 0.0050 wt %, preferably C: not more than 0.0030 wt %, S: not more than 0.0020 wt % and O: not more than 0.0040 wt %.

Si: not more than 3 wt %;

Si is an element effective for the increase of strength in steel, improvement of oxidation resistance, reduction of oxygen amount in steel and stabilization of ferrite phase. However, when the Si amount exceeds 3 wt %, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the Si amount is restricted to not more than 3 wt %. Moreover, the above effect appears in the amount of not less than 0.05 wt % and becomes clear in the amount of not less than 0.1 wt %.

Mn: not more than 5 wt % (ferritic), Mn: not more than 20 wt % (austenitic, dual-phase);

Mn is an element effective for the increase of strength and improvement of hot workability in ferritic stainless steel. When Mn is included in an amount of more than 5 wt %, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amount is restricted to not more than 5 wt %. Moreover, the effect of Mn appears in an amount of not less than 0.05 wt % in the ferritic stainless steel.

Further, Mn is an element effective for not only the increase of strength and improvement of hot workability but also the stabilization of austenite phase in austenitic stainless steel or dual-phase stainless steel. When Mn is included in an amount of more than 20 wt %, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer likewise the above case, so that the amount is restricted to not more than 20 wt %. Moreover, the effect of Mn appears in an amount of not less than 0.10 wt % in the austenitic stainless steel or dual-phase stainless steel.

Cr: 9-50 wt %;

Cr is an element for the improvement of corrosion resistance, but does not contribute to improve the corrosion resistance at an amount of less than 9 wt %. On the other hand, when Cr is included in an amount of more than 50 wt %, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors

other than the Cr-removed layer, so that the amount is restricted to not more than 50 wt %.

Moreover, it is preferable that the amount is 12-30 wt % from a viewpoint of the corrosion resistance and productivity.

Ni: less than 5 wt % (ferritic), 5-20 wt % (austenitic, dual-phase);

Ni is an element effective for improving workability, oxidation resistance and toughness in ferritic stainless steel, so that it may be included in an amount of not less than about 0.1 wt %. However, when it is included in an amount of not less than 5 wt %, martensite phase is formed and the steel becomes considerably brittle, so that the amount is restricted to less than 5 wt %.

Further, Ni is an element required for not only the improvement of workability, corrosion resistance and toughness but also the stabilization of austenite phase in austenitic stainless steel and dual-phase stainless steel. When the Ni amount is less than 5 wt %, the effect is not obtained, while when it exceeds 20 wt %, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amount is restricted to not more than 20 wt %.

N: not more than 0.2000 wt % (austenitic, dual-phase);

N is an element effective for the increase of strength and improvement of corrosion resistance in steel and the stabilization of austenite phase in austenitic stainless steel and dual phase stainless steel. When it is included in an amount of more than 0.2000 wt %, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amount is restricted to not more than 0.2000 wt %. Moreover, the above effect appears in an amount of not less than about 0.01 wt %. And also, the N amount in ferritic stainless steel is desirable to be not more than 0.02 wt %.

In the invention, one or more elements selected from Ti: 0.01-1.0 wt %, Nb: 0.01-1.0 wt %, V: 0.01-1.0 wt %, Zr: 0.01-1.0 wt %, Ta: 0.01-1.0 wt %, Co: 0.1-5 wt %, Cu: 0.1-5 wt %, Mo: 0.1-5 wt %, W: 0.1-5 wt %, Al: 0.01-1.0 wt %, Ca: 0.0003-0.0100 wt % and B: 0.0003-0.0100 wt % may further be included into the above ferritic stainless steel, austenitic stainless steel and dual-phase stainless steel. The reason of these limitations will be described below.

① Ti: 0.01-1.0 wt %, Nb: 0.01-1.0 wt %, V: 0.01-1.0 wt %, Zr: 0.01-1.0 wt %, Ta: 0.01-1.0 wt %;

These elements are added to fix C, N in steel to provide good mechanical properties. This effect is obtained in Ti: not less than 0.01 wt %, Nb: not less than 0.01 wt %, V: not less than 0.01 wt %, Zr: not less than 0.01 wt %, Ta: not less than 0.01 wt %. When the amounts of these elements are too large, the unevenness after annealing-pickling increases due to the increase of surface defects in the steel-making and hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amounts are restricted to Ti: not more than 1.0 wt %, Nb: not more than 1.0 wt %, V: not more than 1.0 wt %, Zr: not more than 1.0 wt %, Ta: not more than 1.0 wt %. Preferably, they are Ti: 0.01-0.6 wt %, Nb: 0.01-0.6 wt %, V: 0.01-0.6 wt %, Zr: 0.01-0.6 wt %, Ta: 0.01-0.6 wt %.

Moreover, each element in this element group has function and effect substantially common to those of the following element groups, so that substantially the same function and effect are developed even in a combination of the other elements when using one of these elements. Therefore, elements in each group will be described together in the following explanation.

② Co: 0.1–5 wt %, Cu: 0.1–5 wt %;

These elements have an effect of improving the workability and toughness in the ferritic stainless steel and have an effect of stabilizing austenite phase to control the formation of strain induced martensite or the like and improving the workability in the austenitic stainless steel and dual-phase stainless steel. These effects are obtained in Co: not more than 0.1 wt %, Cu: not less than 0.1 wt % in any stainless steels. However, when the amounts of these alloying elements are too large, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amounts are restricted to Co: not more than 5 wt %, Cu: not more than 5 wt %.

③ Mo: 0.1–5 wt %, W: 0.1–5 wt %;

These elements have an effect of improving the corrosion resistance of stainless steel. This effect is obtained in Mo: not less than 0.1 wt %, W: not less than 0.1 wt %. However, when the amounts of these alloying elements are too large, the unevenness after annealing-pickling increases due to the increase of surface defects in the hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amounts are restricted to Mo: not more than 5 wt %, W: not more than 5 wt %.

④ Al: 0.005–5.0 wt %;

Al has an effect for improving not only the oxidation resistance of steel but also the strength. This effect is obtained in an amount of not less than 0.005 wt %. However, when the Al amount is too large, the unevenness after annealing-pickling increases due to the increase of surface defects in the steel-making and hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amount is restricted to not more than 5.0 wt %.

⑤ Ca: 0.0003–0.0100 wt %;

Ca has an effect of controlling the form of inclusion in steel and the strength to improve the mechanical properties and toughness. This effect is obtained in an amount of not less than 0.0003 wt %. However, when the addition amount is too large, the unevenness after annealing-pickling increases due to the increase of surface defects in the steel-making and hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amount is restricted to not more than 0.0100 wt %.

⑥ B: 0.0003–0.0100 wt %;

B has an effect of causing segregation in grain boundary to increase the strength of grain boundary and improve secondary work brittleness. This effect is obtained in an amount of not less than 0.0003 wt %. However, when the addition amount is too large, the unevenness after annealing-pickling increases due to the increase of surface defects in the steel-making and hot rolling and the degradation of corrosion resistance is caused by factors other than the Cr-removed layer, so that the amount is restricted to not more than 0.0100 wt %.

Particularly, the other components are not necessarily restricted, but it is desirable that P is not more than 0.05 wt %.

As the above selective addition elements in the invention, it is effective to use elements in each group of ①–⑥ alone

or add a combination of 2 or more elements selected from the groups of ①–⑥.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing a relation between draft below 830° C. and rust generating area ratio in SUS 304 stainless steel.

FIG. 2 is a graph showing a relation between draft below 830° C. and rust generating area ratio in SUS 430 stainless steel.

FIG. 3 is a graph showing a relation between cooling rate after the completion of hot rolling and rust generating area ratio in SUS 304 stainless steel.

FIG. 4 is a graph showing a relation between cooling rate after the completion of hot rolling and rust generating area ratio in SUS 430 stainless steel.

FIG. 5 is a graph showing a relation between coiling temperature and rust generating area ratio in SUS 304 stainless steel.

FIG. 6 is a graph showing a relation between coiling temperature and rust generating area ratio in SUS 430 stainless steel.

BEST MODE FOR CARRYING OUT THE INVENTION

Each of stainless steels having chemical compositions shown in Tables 1 to 4 (In a column of kind of steel in each Table, F is ferritic, A is austenitic and D is dual-phase) is melted in a converter, subjected to degassing by VOD process and adjustment of slight components, and continuously cast into a slab of 200 mm in thickness.

Then, the slab is reheated at 1200° C. for 2 hours, rough-rolled to a thickness of 10–20 mm, and further continuously finish rolled to obtain a hot rolled sheet having a thickness of 0.9–4 mm. This hot rolling step is carried out under various conditions of draft below 830° C., finish temperature of hot rolling, cooling rate and coiling temperature.

After the hot rolling, the hot rolled sheets No. 1–49, 90, 92 and 94–98 are subjected to a continuous annealing in which they are heated at 1150° C. in a butane burning atmosphere for 1 minute and cooled to room temperature with water, and the hot rolled sheets No. 50–56, No. 72, 80, 81 and 93 are subjected to a continuous annealing in which they are heated at 1000° C. in a butane burning atmosphere for 1 minute and cooled to room temperature with water, and the hot rolled sheets No. 57–71, 73–79, 82–89, 91, 95 and 99–101 are subjected to a batch annealing in which they are heated at 850° C. in an atmosphere of H₂ gas: 5% and the remainder: N₂ gas having a dew point of –30° C. for 5 hours and gradually cooled to room temperature. Thereafter, the annealed sheets are subjected to a mechanical preliminary descaling with shot blast, immersed in an aqueous solution of 80° C. containing H₂SO₄: 200 g/l (0.2 g/cm³) for 10 seconds and then immersed in an aqueous solution of 60° C. containing HF: 25 g/l (0.025 g/cm³) and HNO₃: 150 g/l (0.150 g/cm³) for 10 seconds and washed with water to complete pickling and descaling.

TABLE 1

Kind of		Chemical composition (wt %)									
No.	steel	C	S	O	Si	Mn	Cr	Ni	N	P	others
1	A	0.0042	0.0038	0.0025	0.62	1.22	17.1	7.0	0.1081	0.0274	0.06 Nb, 0.60 Cu
2	A	0.0012	0.0035	0.0038	0.57	1.03	17.7	8.8	0.0248	0.0332	
3	A	0.0018	0.0038	0.0011	0.56	1.05	18.4	8.7	0.0372	0.0330	
4	A	0.0055	0.0031	0.0007	0.55	1.00	17.8	8.5	0.0387	0.0329	0.30 Cu
5	A	0.0049	0.0039	0.0034	0.55	1.01	18.0	8.5	0.0386	0.0334	0.30 Cu
6	A	0.0041	0.0011	0.0012	0.55	1.03	18.4	8.3	0.0377	0.0330	1.0 Cu
7	A	0.0053	0.0039	0.0033	0.57	1.02	18.5	9.2	0.0315	0.0337	0.30 Cu
8	A	0.0005	0.0015	0.0008	0.44	1.37	17.9	8.3	0.0372	0.0314	0.20 Ti, 0.30 Cu
9	A	0.0018	0.0016	0.0032	0.44	1.38	18.0	8.2	0.0370	0.0315	0.20 Ti
10	A	0.0013	0.0025	0.0026	0.46	1.36	17.6	8.2	0.0371	0.0319	0.20 Ti, 0.30 Cu
11	A	0.0037	0.0018	0.0008	0.54	0.99	17.9	8.3	0.0377	0.0032	0.30 Cu
12	A	0.0014	0.0031	0.0011	0.54	1.51	18.6	9.3	0.0357	0.0311	
13	A	0.0013	0.0023	0.0024	0.61	1.19	18.4	8.9	0.0375	0.0251	0.090 Al
14	A	0.0041	0.0014	0.0023	0.58	1.68	18.7	9.7	0.0247	0.0243	0.025 Ti
15	A	0.0026	0.0009	0.0038	0.60	1.66	18.0	11.0	0.0249	0.0248	
16	A	0.0044	0.0016	0.0034	0.39	1.70	18.1	11.2	0.0249	0.0245	0.025 Al
17	A	0.0009	0.0007	0.0021	0.41	1.67	17.8	11.3	0.0252	0.0301	0.1 Al
18	A	0.0021	0.0024	0.0035	0.59	1.29	16.5	10.6	0.0245	0.0329	0.020 Ti, 2.20 Mo, 0.0030 B
19	A	0.0046	0.0009	0.0037	0.58	1.33	16.2	12.3	0.0251	0.0327	0.020 Ti, 2.20 Mo
20	A	0.0031	0.0029	0.0037	0.59	1.48	14.4	15.4	0.0380	0.0244	0.08 Al
21	A	0.0038	0.0033	0.0022	0.41	0.70	16.7	7.1	0.0255	0.0245	1.04 Al
22	A	0.0035	0.0014	0.0009	0.80	1.56	24.1	19.3	0.0255	0.0298	
23	A	0.0023	0.0007	0.0038	0.45	1.36	18.1	8.4	0.0379	0.0324	0.02 Nb
24	D	0.0052	0.0037	0.0022	0.45	1.34	46.7	18.7	0.0378	0.0326	0.02 V
25	A	0.0046	0.0016	0.0029	0.44	1.37	18.6	8.6	0.0389	0.0316	0.05 Ta

TABLE 2

Kind of		Chemical composition (wt %)									
No.	steel	C	S	O	Si	Mn	Cr	Ni	N	P	others
26	A	0.0042	0.0035	0.0013	0.46	1.31	17.6	8.3	0.0375	0.0322	0.08 Zr
27	A	0.0047	0.0018	0.0039	0.46	1.38	18.2	8.2	0.0374	0.0319	0.30 Co
28	A	0.0040	0.0026	0.0030	0.59	1.26	16.7	11.9	0.0253	0.0340	3.0 Mo
29	A	0.0043	0.0035	0.0008	0.61	1.30	15.9	12.1	0.0246	0.0335	3.0 N
30	A	0.0039	0.0023	0.0038	0.62	1.28	16.3	10.3	0.0251	0.0335	0.0030 B
31	A	0.0021	0.0018	0.0017	0.54	1.00	18.0	8.5	0.0289	0.0330	0.0030 Ca
32	A	0.0038	0.0037	0.0025	0.55	1.04	18.6	8.3	0.0385	0.0328	0.30 Cu, 0.0030 Ca
33	A	0.0045	0.0037	0.0023	0.48	0.98	16.8	7.9	0.0374	0.0338	0.20 Ti, 0.02 Al, 0.0018 Ca
34	A	0.0018	0.0030	0.0007	0.51	0.95	17.1	8.8	0.0412	0.0334	0.20 Ti, 0.01 Al, 0.0011 B
35	A	0.0044	0.0012	0.0032	0.59	1.35	18.5	8.1	0.0219	0.0316	0.20 Ti, 0.01 Al, 0.0020 Ca, 0.0010 B
36	A	0.0048	0.0015	0.0028	0.53	0.98	16.1	10.4	0.0355	0.0313	0.20 Ti, 0.01 Al, 0.0020 Ca, 2.5 Mo
37	A	0.0018	0.0026	0.0024	0.56	1.05	17.4	10.1	0.0415	0.0310	0.20 Ti, 0.02 Al, 0.0015 B, 2.5 Mo
38	A	0.0038	0.0031	0.0037	0.58	1.12	16.5	10.3	0.0255	0.0319	0.20 Ti, 0.02 Al, 0.0021 Ca, 0.0009 B, 2.5 Mo
39	A	0.0013	0.0015	0.0038	0.55	1.17	19.8	7.4	0.0240	0.0297	0.20 Ti, 0.01 Al, 0.30 Cu
40	A	0.0025	0.0017	0.0010	0.52	0.95	16.8	7.8	0.0390	0.0303	0.21 Ti, 0.01 Al, 0.0022 Ca, 0.30 Cu
41	A	0.0009	0.0024	0.0031	0.54	0.98	20.5	9.1	0.0357	0.0317	0.20 Ti, 0.01 Al, 0.0010 B, 0.30 Cu
42	A	0.0043	0.0027	0.0030	0.61	1.05	17.6	9.0	0.0382	0.0292	0.21 Ti, 0.01 Al, 0.0023 Ca, 0.0015 B, 0.30 Cu
43	A	0.0036	0.0023	0.0014	0.48	1.02	18.4	8.4	0.0370	0.0262	0.19 Ti, 0.0008 Ca
44	A	0.0049	0.0029	0.0040	0.52	1.02	16.3	8.8	0.0357	0.236	0.20 Ti, 0.0010 B
45	A	0.0022	0.0031	0.0009	0.55	1.02	15.2	10.3	0.0401	0.0279	0.20 Ti, 0.0020 Ca, 2.0 Mo
46	A	0.0018	0.0017	0.0014	0.56	0.93	17.0	10.0	0.0346	0.0272	0.20 Ti, 0.0021 Ca, 0.0010 B, 2.0 Mo
47	A	0.0049	0.0021	0.0033	0.52	1.12	16.6	8.8	0.0367	0.0267	0.20 Ti, 0.0020 Ca, 0.16 Cu
48	A	0.0028	0.0030	0.0034	0.57	0.92	16.9	9.0	0.0349	0.0251	0.20 Ti, 0.0010 B, 1.0 Cu
49	A	0.0032	0.0013	0.0023	0.51	0.92	17.7	9.0	0.0418	0.0282	0.20 Ti, 0.0020 Ca, 0.0014 B, 1.0 Cu

TABLE 3

Kind of		Chemical composition (wt %)									
No.	steel	C	S	O	Si	Mn	Cr	Ni	N	P	others
50	F	0.0013	0.0015	0.0037	0.50	0.43	11.8	—	0.0083	0.0270	0.20 Ti, 0.01 Al, 0.30 Cu
51	F	0.0025	0.0017	0.0009	0.54	0.53	11.8	—	0.0071	0.0272	0.21 Ti, 0.01 Al, 0.0022 Ca, 0.30 Cu
52	F	0.0009	0.0025	0.0031	0.41	0.54	11.5	—	0.0089	0.0183	0.20 Ti, 0.01 Al, 0.0010 B, 0.30 Cu
53	F	0.0043	0.0027	0.0030	0.46	0.43	11.6	—	0.0089	0.0256	0.21 Ti, 0.01 Al, 0.0023 Ca, 0.0015 B, 0.30 Cu
54	F	0.0047	0.0022	0.0032	0.58	0.47	11.6	—	0.0087	0.0203	0.20 Ti, 0.0020 Ca, 0.16 Cu
55	F	0.0029	0.0032	0.0033	0.50	0.41	11.9	—	0.0074	0.0279	0.20 Ti, 0.0010 B, 1.0 Cu
56	F	0.0031	0.0013	0.0024	0.50	0.54	11.7	—	0.0072	0.0243	0.20 Ti, 0.0020 Ca, 0.0014 B, 1.0 Cu
57	F	0.0008	0.0034	0.0014	0.31	0.59	16.2	—	0.0046	0.0309	
58	F	0.0049	0.0029	0.0027	0.32	0.60	16.4	—	0.0054	0.0299	0.012 Al
59	F	0.0006	0.0029	0.0037	0.32	0.66	15.9	0.3	0.0038	0.0300	0.012 Al
60	F	0.0025	0.0018	0.0035	0.39	0.64	16.4	—	0.0034	0.0301	0.07 Al
61	F	0.0026	0.0021	0.0028	0.88	0.92	17.1	0.5	0.0049	0.0297	0.065 Al
62	F	0.0044	0.0030	0.0009	0.54	0.65	15.8	—	0.0040	0.0306	0.012 Al
63	F	0.0027	0.0015	0.0021	0.10	0.31	16.8	—	0.0050	0.0347	0.01 Al, 0.22 Nb, 0.85 Mo
64	F	0.0025	0.0022	0.0013	0.10	0.30	16.3	—	0.0051	0.0354	0.22 Nb, 0.85 Mo, 0.065 Al
65	F	0.0037	0.0020	0.0032	0.10	0.30	18.1	—	0.0049	0.0346	0.27 Nb, 1.80 Mo, 0.05 Al
66	F	0.0045	0.0028	0.0038	0.29	0.15	18.6	—	0.0051	0.0343	0.35 Nb, 1.90 Mo, 0.01 Al
67	F	0.0005	0.0010	0.0033	0.25	0.30	18.0	—	0.0131	0.0356	0.38 Nb, 0.55 Mo, 0.03 Al
68	F	0.0019	0.0033	0.0013	0.40	0.30	16.9	—	0.0141	0.0360	0.42 Nb, 0.01 Al
69	F	0.0036	0.0008	0.0030	0.40	0.30	18.3	—	0.0140	0.0360	0.47 Nb, 0.01 Al
70	F	0.0026	0.0017	0.0035	0.06	0.15	17.4	—	0.0082	0.0256	1.20 Mo, 0.27 Ti, 0.025 Al
70	F	0.0042	0.0022	0.0040	0.06	0.15	17.6	—	0.0081	0.0249	1.20 Mo, 0.27 Ti, 0.025 Al
72	F	0.0019	0.0021	0.0010	0.20	0.10	29.5	0.3	0.0071	0.0183	0.14 Nb, 1.85 Mo, 0.1 Al
73	F	0.0051	0.0026	0.0024	0.50	0.49	10.9	—	0.0082	0.0257	0.25 Ti, 0.03 Al
74	F	0.0035	0.0032	0.0021	0.35	0.24	11.1	—	0.0082	0.0171	0.22 Ti, 0.07 V, 0.025 Al
75	F	0.0039	0.0013	0.0013	0.25	0.30	10.8	—	0.0098	0.0198	0.25 Ti, 0.02 Al

TABLE 4

Kind of		Chemical composition (wt %)									
No.	steel	C	S	O	Si	Mn	Cr	Ni	N	P	others
76	F	0.0034	0.0014	0.0006	0.38	0.25	11.2	—	0.0091	0.0306	0.31 Ti, 0.045 Al
77	F	0.0008	0.0008	0.0032	0.24	0.29	10.9	—	0.0072	0.0177	0.25 Ti, 0.02 Al
78	F	0.0028	0.0009	0.0023	0.25	0.31	10.8	—	0.0070	0.0249	0.25 Ti, 0.02 Al
79	F	0.0017	0.0036	0.0012	0.40	0.29	17.4	—	0.0141	0.0358	0.10 V
80	F	0.0051	0.0019	0.0022	0.20	0.10	45.2	0.3	0.0068	0.0181	0.10 Zr
81	F	0.0041	0.0023	0.0019	0.20	0.10	45.6	0.3	0.0071	0.0183	0.10 Zr, 1.85 Mo
82	F	0.0018	0.0009	0.0019	0.39	0.31	17.4	—	0.0141	0.0360	0.08 Ta
83	F	0.0051	0.0039	0.0013	0.40	0.30	17.3	—	0.0144	0.0351	0.5 Cu
84	F	0.0023	0.0010	0.0009	0.40	0.31	17.1	—	0.0138	0.0348	0.5 Co
85	F	0.0042	0.0009	0.0030	0.10	0.31	17.6	—	0.0050	0.0346	1.2 Mo
86	F	0.0053	0.0005	0.0011	0.10	0.30	17.5	—	0.0050	0.0344	1.5 W
87	F	0.0025	0.0017	0.0018	0.50	0.49	11.4	—	0.0082	0.0244	0.0030 B
88	F	0.0035	0.0013	0.0036	0.49	0.51	11.3	—	0.0081	0.0248	0.0030 Ca
89	F	0.0020	0.0040	0.0038	0.49	0.49	11.4	—	0.0079	0.0256	0.25 Ti, 0.0030 B, 0.0030 Ca
90	A	0.0033	0.0014	0.0019	0.55	1.55	18.1	9.3	0.0349	0.0311	
91	F	0.0010	0.0007	0.0038	0.10	0.30	16.9	—	0.0050	0.0351	0.22 Nb, 0.85 Mo
92	A	0.0020	0.0006	0.0017	0.60	1.26	16.7	12.3	0.0244	0.0325	0.020 Ti, 2.20 Mo
93	F	0.0037	0.0036	0.0023	0.20	0.10	29.9	0.3	0.0071	0.0179	0.14 Nb, 1.85 Mo
94	A	0.0024	0.0016	0.0022	0.56	1.03	18.3	8.3	0.0374	0.0339	0.30 Cu
95	F	0.0010	0.0032	0.0031	0.26	0.30	10.9	—	0.0068	0.0178	0.25 Ti
96	A	0.0400	0.0026	0.0026	0.55	1.00	18.3	8.2	0.0390	0.0338	0.30 Cu
97	A	0.0046	0.0068	0.0022	0.44	1.32	17.8	8.4	0.0385	0.0313	0.20 Ti, 0.30 Cu
98	A	0.0011	0.0010	0.0071	0.46	1.34	18.0	8.3	0.0387	0.0311	0.20 Ti
99	F	0.0215	0.0035	0.0040	0.25	0.31	11.2	—	0.0071	0.0251	0.25 Ti
100	F	0.0023	0.0078	0.0015	0.06	0.15	17.8	—	0.0080	0.0254	1.20 Mo, 0.27 Ti
101	F	0.0042	0.0019	0.0083	0.06	0.15	17.7	—	0.0078	0.0248	1.20 Mo, 0.27 Ti

Each test specimens of ① as-hot-rolled, ② subjected to 10% skin pass rolling or ③ further subjected to cold rolling are made from the above hot rolled sheets and then subjected to a test for corrosion resistance.

Moreover, the test specimen ② is made from only the hot rolled sheets having a thickness of not more than 1.5 mm. Further, the test specimen ③ is made by the following method. That is, the hot rolled sheets are subjected to a cold

60 rolling at various drafts in a tandem rolling mill comprising rolls of 250 mm in diameter. Then, the cold rolled sheets No. 1-32, 66, 68, 70, 72-74 are subjected to an annealing in which they are heated at 1150° C. in a butane gas burning atmosphere for 10 seconds and cooled in air to room temperature. Thereafter, they are subjected to an electrolysis in an aqueous solution of 80° C. neutral salt containing Na₂SO₄: 200 g/l at a current density: 10 A/dm² for 40

seconds so as to dissolve the steel sheet at anode, immersed in an aqueous solution of 60° C. containing HF: 25 g/l (0.025 g/cm³), HNO₃: 55 g/l (0.055 g/cm³) for 10 seconds, and subjected to an electrolysis in an aqueous solution containing HNO₃: 100 g/l (0.100 g/cm³) at a current density: 10 A/dm² to passivate the steel sheet. The cold rolled sheets No. 33-65, 67, 69, 71, 75-77 are subjected to a bright annealing by heating at 900° C. in an ammonia decomposed gas for 10 seconds.

Tables 5-8 show not only the thickness of hot rolled sheet but also draft below 830° C., finish temperature of hot rolling, cooling rate, coiling temperature and draft of cold rolling through work rolls having a diameter of 250 mm.

TABLE 5

No.	Hot rolling					Rust generating area				Remarks
	Draft	Temperature	Cooling rate °C./sec	Coiling tempera- ture (°C.)	Thickness of hot rolled sheet (mm)	Draft	ratio (%)			
	below 830° C. (%)	at completion of rolling (°C.)				Hot rolled sheet	Hot rolled skinpass sheet	Cold rolled sheet		
1	36	720	93	464	2.2	64	0.5	—	0.4	Invention process
2	32	690	44	523	2.1	76	2.0	—	1.4	
3	36	780	31	609	3.9	79	4.0	—	2.7	
4	38	810	50	497	3.5	77	1.1	—	0.8	
5	33	690	83	269	2.4	67	0.1	—	0.0	
6	38	810	31	508	1.7	53	1.6	—	1.1	
7	35	720	47	390	2.4	67	0.6	—	0.5	
8	34	810	56	462	1.8	56	0.3	—	0.2	
9	35	810	49	639	3.8	79	2.9	—	1.8	
10	37	780	100	642	2.2	64	1.2	—	0.8	
11	30	720	54	165	0.9	25	0.0	0.0	0.0	
12	32	720	42	459	2.2	64	0.7	—	0.5	
13	38	690	69	213	3.7	78	0.0	—	0.0	
14	39	720	95	534	3.8	79	0.6	—	0.4	
15	39	750	92	477	1.2	33	0.4	0.4	0.3	
16	39	780	71	396	3.3	76	0.3	—	0.2	
17	39	810	51	224	0.9	25	0.0	0.0	0.0	
18	35	810	50	439	3.3	76	0.3	—	0.2	
19	35	690	93	433	3.1	74	0.2	—	0.1	
20	33	780	48	412	3.6	78	0.6	—	0.5	
21	30	720	84	491	4.0	80	0.8	—	0.6	
22	33	810	82	529	1.6	50	0.7	—	0.4	
23	30	720	74	623	3.4	76	1.6	—	1.1	
24	33	750	55	548	2.1	62	1.4	—	1.1	
25	35	690	28	378	2.4	67	0.9	—	0.7	

45

TABLE 6

No.	Hot rolling					Rust generating area				Remarks
	Draft	Temperature	Cooling rate °C./sec	Coiling tempera- ture (°C.)	Thickness of hot rolled sheet (mm)	Draft	ratio (%)			
	below 830° C. (%)	at completion of rolling (°C.)				Hot rolled sheet	Hot rolled skinpass sheet	Cold rolled sheet		
26	48	780	56	255	2.4	67	0.0	—	0.0	Invention process
27	31	750	82	325	2.0	60	0.1	—	0.1	
28	39	780	39	206	1.0	21	0.0	0.0	0.0	
29	38	780	40	510	2.5	68	0.8	—	0.5	
30	34	810	71	479	3.1	74	0.8	—	0.6	
31	34	810	56	248	2.0	60	0.0	—	0.0	
32	32	780	53	403	1.1	27	0.6	0.4	0.4	
33	35	804	42	571	3.0	50.0	1.0	—	0.5	
34	31	824	50	551	2.5	72.0	0.8	—	0.2	
35	36	824	51	596	3.0	76.7	0.8	—	0.2	

TABLE 6-continued

Hot rolling						Rust generating area				Remarks
No.	Draft	Temperature	Cooling rate °C./sec	Coiling tempera- ture (°C.)	Thickness of hot rolled sheet (mm)	Draft in cold rolling (%)	ratio (%)			
	below 830° C. (%)	at completion of rolling (°C.)					Hot rolled sheet	Hot rolled skinpass sheet	Cold rolled sheet	
36	31	817	42	551	3.0	76.7	0.2	—	0.0	
37	34	805	37	618	2.5	40.0	0.2	—	0.1	
38	31	821	48	609	3.0	50.0	0.2	—	0.1	
39	30	825	35	609	3.0	50.0	0.8	—	0.4	
40	33	811	39	638	2.5	40.0	0.6	—	0.3	
41	34	808	47	590	2.0	50.0	0.7	—	0.4	
42	34	827	42	602	3.0	50.0	0.9	—	0.5	
43	36	822	33	618	2.0	65.0	0.7	—	0.3	
44	32	827	43	554	3.0	50.0	0.9	—	0.4	
45	33	805	36	584	3.0	76.7	0.2	—	0.0	
46	32	816	48	562	2.5	72.0	0.1	—	0.0	
47	35	812	41	589	3.0	66.7	0.7	—	0.2	
48	32	810	38	619	3.0	50.0	1.0	—	0.5	
49	30	824	36	621	3.0	76.7	0.8	—	0.2	

TABLE 7

No.	Hot rolling					Rust generating area				Remarks
	Draft	Temperature	Cooling rate °C./sec	Coiling tempera- ture (°C.)	Thickness of hot rolled sheet (mm)	Draft in cold rolling (%)	ratio (%)			
	below 830° C. (%)	at completion of rolling (°C.)					Hot rolled sheet	Hot rolled skinpass sheet	Cold rolled sheet	
50	30	802	40	558	3.0	66.7	1.5	—	0.5	Invention process
51	31	788	30	558	3.0	66.7	1.2	—	0.4	
52	34	790	35	560	3.0	66.7	1.3	—	0.4	
53	32	754	33	580	3.0	66.7	1.8	—	0.6	
54	32	800	32	600	3.0	66.7	2.1	—	0.7	
55	30	768	38	610	3.0	66.7	1.9	—	0.6	
56	35	777	35	562	3.0	66.7	2.0	—	0.7	
57	31	750	72	376	3.1	74	0.2	—	0.2	
58	33	810	89	648	3.8	79	3.5	—	2.6	
59	36	810	61	407	3.1	74	0.4	—	0.3	
60	36	690	56	272	3.4	76	0.1	—	0.0	
61	31	750	56	635	1.7	53	3.8	—	2.5	
62	35	720	79	623	2.1	62	2.5	—	1.6	
63	36	690	94	388	2.2	64	0.1	—	0.1	
64	40	810	77	323	3.7	78	0.0	—	0.0	
65	31	750	78	453	2.2	64	0.4	—	0.3	
66	37	750	51	186	2.7	70	0.0	—	0.0	
67	31	750	46	258	3.7	78	0.0	—	0.0	
68	39	780	55	250	1.5	47	0.0	0.0	0.0	
69	37	780	100	220	2.8	71	0.0	—	0.0	
70	35	780	37	436	1.0	50	0.5	0.5	0.4	
71	39	750	60	180	3.1	74	0.0	—	0.0	
72	33	720	55	183	1.9	58	0.0	—	0.0	
73	32	810	96	151	3.4	76	0.0	—	0.0	
74	38	750	45	596	2.3	65	3.6	—	2.3	
75	30	750	48	428	2.0	60	0.7	—	0.5	

TABLE 8

No.	Hot rolling					Rust generating area				Remarks
	Draft	Temperature	Cooling rate °C./sec	Coiling temperature (°C.)	Thickness of hot rolled sheet (mm)	Draft	ratio (%)			
	below 830° C. (%)	at completion of rolling (°C.)				Hot rolled sheet	Hot rolled skinpass sheet	Cold rolled sheet		
76	32	780	85	500	1.3	38	0.6	0.5	0.4	Invention process
77	33	720	68	436	1.4	43	0.3	0.3	0.3	
78	33	810	71	461	3.6	78	0.5	—	0.3	
79	30	690	31	589	3.2	75	4.6	—	3.2	
80	31	720	77	207	1.0	30	0.0	0.0	0.0	
81	38	720	40	270	3.9	79	0.1	—	0.0	
82	48	690	50	414	1.8	56	0.2	—	0.2	
83	36	810	28	191	1.6	50	0.0	—	0.0	
84	40	720	64	630	3.8	79	1.2	—	0.8	
85	37	710	31	441	2.4	67	0.7	—	0.5	
86	34	810	57	512	2.0	60	0.6	—	0.4	Compara- tive process
87	31	810	30	377	1.9	58	0.6	—	0.4	
88	37	720	88	634	1.8	56	2.1	—	1.6	
89	32	810	39	190	2.9	72	0.0	—	0.0	
90	0	850	37	602	2.4	67	18.5	—	12.3	
91	17	800	29	616	3.2	75	12.2	—	7.7	
92	32	760	12	648	2.5	68	13.5	—	10.4	
93	0	900	6	740	4.0	75	50.4	—	34.9	
94	33	810	29	731	2.9	72	12.1	—	8.9	
95	31	690	31	746	0.9	40	14.7	12.6	10.3	
96	34	800	25	621	2.1	62	41.5	—	29.6	
97	33	700	39	608	1.3	38	14.5	—	11.3	
98	31	800	30	643	3.1	74	11.2	—	8.7	
99	34	700	35	617	2.6	69	19.6	—	12.5	
100	31	750	35	602	1.2	33	13.8	12.5	9.5	
101	33	800	40	625	2.3	65	12.5	—	8.9	

The corrosion resistance is examined with respect to the test specimens made by the above method. That is, CCT test of spraying an aqueous solution of 35° C. containing NaCl: 5% for 4 hours, drying for 2 hours and holding in a wet atmosphere for 2 hours as one cycle is conducted, and the degree of rust generation after 2 days is compared. The results are also shown in Tables 5-8.

The sheets No. 1-89 according to the invention process exhibit good corrosion resistance because the rust generating area ratio is not more than 5% in all of hot rolled sheets, hot rolled-skin pass rolled sheets and cold rolled sheets. On the contrary, the rust generating area ratio exceeds 5% in the sheets No. 90, 91, 93 wherein the draft below 830° C. is less than 30%, the sheets No. 92, 93 wherein the cooling rate is less than 25° C./sec, the sheets No. 93, 94, 95 wherein the coiling temperature exceeds 650° C. and the sheets No. 96-101 wherein the production conditions are within the ranges defined in the invention but the C, S, O amounts are too high, so that these sheets are poor in the corrosion resistance.

INDUSTRIAL APPLICABILITY

As mentioned above, according to the invention, the starting material containing C: not more than 0.100 wt %, S: not more than 0.0050 wt % and O: not more than 0.0050 wt % is hot rolled at a draft below 830° C. of not less than 30%, cooled at a cooling rate of not less than 25° C./sec and coiled below 650° C., whereby the growth of Cr-removed layer in the annealing, which has been come into problem in stainless steels having extreme-low amounts of C, S and O, can be controlled and the surface chapping of the steel sheet in subsequent pickling can be prevented. Consequently, it is possible to considerably improve the corrosion resistance of the extreme-low C, S, O stainless steel sheet, and particu-

larly this effect becomes large when the sheet is finished by skin pass rolling after hot rolling-annealing-pickling, or when cold rolling is conducted through large size rolls.

Furthermore, according to the invention, the surface defects can considerably be reduced, so that there are provided cold rolled sheets having a beautiful surface and a good gloss.

We claim:

1. A process for the production of stainless steel sheets having an excellent corrosion resistance, wherein said stainless steel sheet contains C: not more than 0.01 wt %, S: not more than 0.005 wt % and O: not more than 0.005 wt % said stainless steel being produced by the steps of:

hot rolling said stainless steel sheet at a draft below 830° C. of greater than about 30%,

cooling the resulting hot rolled sheet at a cooling rate of greater than about 25° C./sec,

coiling said stainless steel sheet at a temperature of less than about 650° C., and thereafter subjecting said stainless steel sheet to annealing and pickling.

2. The process for the production of stainless steel sheets of claim 1, further comprising the step of skin pass rolling said stainless steel sheet at a draft of less than about 20%.

3. The process for the production of stainless steel sheets of claim 1, wherein said stainless steel sheet is further subjected to a cold rolling at a total draft of more than about 20% with work rolls having a roll diameter of greater than about 250 mm.

4. A process according to anyone of claims 1 to 3, wherein said stainless steel sheet is a ferritic stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 5 wt %, Cr: 9-50 wt %, Ni: less than 5 wt %, and the remainder being Fe and inevitable impurities.

5. A process according to anyone of claims 1 to 3, wherein said stainless steel sheet is a ferritic stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 5 wt %, Cr: 9–50 wt %, Ni: less than 5 wt %, and further containing one or more elements selected from the group consisting of Ti: 0.01–1.0 wt %, Nb: 0.01–1.0 wt %, V: 0.01–1.0 wt %, Zr: 0.01–1.0 wt %, Ta: 0.01–1.0 wt %, Co: 0.1–5 wt %, Cu: 0.1–5 wt %, Mo: 0.1–5 wt %, W: 0.1–5 wt %, Al: 0.005–5.0 wt %, Ca: 0.0003–0.01 wt % and B: 0.0003–not more than 0.01 wt %, and the remainder being Fe and inevitable impurities.

6. A process according to anyone of claims 1 to 3, wherein said stainless steel sheet is selected from the group consisting of an austenitic stainless steel and a dual-phase stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 20 wt %, Cr: 9–50 wt %, Ni: 5–20 wt %, N: not more than 0.2 wt %, and the remainder being Fe and inevitable impurities.

Ni: 5–20 wt %, N: not more than 0.2 wt %, and the remainder being Fe and inevitable impurities.

7. A process according to anyone of claims 1 to 3, wherein said stainless steel sheet is selected from the group consisting of an austenitic stainless steel and a dual-phase stainless steel comprising C: not more than 0.01 wt %, S: not more than 0.005 wt %, O: not more than 0.005 wt %, Si: not more than 3 wt %, Mn: not more than 20 wt %, Cr: 9–50 wt %, Ni: 5–20 wt %, N: not more than 0.2 wt %, and further containing one or more elements selected from the group consisting of Ti: 0.01–1.0 wt %, Nb: 0.01–1.0 wt %, V: 0.01–1.0 wt %, Zr: 0.01–1.0 wt %, Ta: 0.01–1.0 wt %, Co: 0.1–5 wt %, Cu: 0.1–5 wt %, Mo: 0.1–5 wt %, W: 0.1–5 wt %, Al: 0.005–5.0 wt %, Ca: 0.0003–0.01 wt % and B: 0.0003–not more than 0.01 wt %, and the remainder being Fe and inevitable impurities.

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X. RELATED PROCEEDINGS APPENDIX

None.